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Iodine-Promoted Radical Cyclization in Water: A Selective Reaction of 1,6-Enynes with Sulfonyl Hydrazides

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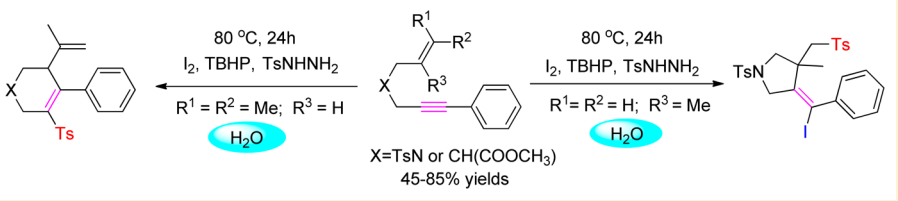
Supporting Information



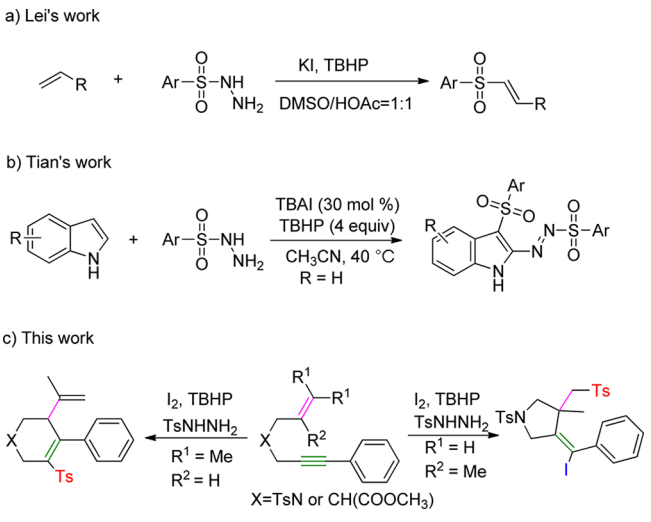
ABSTRACT: An iodine-promoted one-pot radical cyclization reaction of 1,6-enynes with sulfonyl hydrazides to provide five-membered and hexatomic ring sulfonylated products under the same conditions is established. This reaction proceeded smoothly in water and gave the corresponding products by using I_2/TBHP instead of expensive and toxic catalysts with C−S and C−I bond formed in one step. This method also allowed easy access to significant functional sulfones for potential applications in medicinal and organic chemistry.

INTRODUCTION

Reactions referring to the reduction cyclization or cycloisomerization of enynes are quite valuable, as they can generate an array of structurally diverse molecular complexity and prepare cyclic skeletons under mild conditions.[1] Endowed with unsaturated C−C bonds, enynes are desirable to privilege building blocks, and have been extensively devoted to direct and selective tandem cyclizations across C═C and C≡C bond in a one-step operation.[2] For the transition-metal-catalyzed cycloadditions of enynes, the major mechanism involves the formation of metal cyclopropyl carbenes intermediates by 5-*exo* cyclization, which has been widely accepted for the cycloisomerization of 1,6-enynes.[3−7] Among them, a range of well-known reactions concern the alkyne activation of the substrates followed by the addition of the alkene and then convert into cyclic compounds. In this respect, our group has reported the radical cyclization reactions of 1,6-enynes for the synthesis of CF_3-containing heterocycles and phosphorated fluorene derivatives by transition metal catalysis.[8] In addition, the development of metal-free reactions has received a great attention in recent years for its relevance to "green" chemical processes.[9] Efficient and general methodologies for cyclization of enynes under mental-free conditions, therefore, are in high demand. In 2014, a metal-free cascade cyclization of 1,6-enynes with aldehydes to construct tricyclic fluorine derivatives was also developed by our group.[10] Although great achievements have been scored in this field, seeking a novel radical reaction to construct heterocycles with high chemical selectivity via attacking unsaturated bonds of 1,6-enyne is highly desirable.

Owing to the materiality of sulfonyl-containing compounds in medicinal areas, in photovoltaic materials and general synthetic, numerous efforts have been involved in the area on the synthesis of sulfonylated compounds.[11] Lei group has developed an iodide-catalyzed radical alkenylation reaction of sulfonyl hydrazides with simple alkenes (Scheme 1).[12] Recently, Tian and co-workers have reported the reaction of sulfonyl hydrazides with indoles for the synthesis of sulfonylated indoles.[13] We anticipated that under the advisible catalytic conditions, the sulfonyl radical which is emerged from

Scheme 1. Sulfonylated Reactions via Iodine-Promoted Process



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sulfonyl hydrazides could be employed in cascade bond-forming events with terminal alkene, internal C=C or C≡C bond of 1,6-enynes systems.[14,15] According to recent reports, iodine has been shown to be a good additive or catalyst for initiating the sulfonyl radical.[16] Herein we report our progress on the synthesis of sulfonylated cyclic compounds via iodine-promoted process of 1,6-enynes with sulfonyl hydrazides in water. In this report, the radical selectively attacked the C=C bond or C≡C bond of 1,6-enynes resulted in five-membered cyclic compounds or six-membered cyclic compounds, respectively.

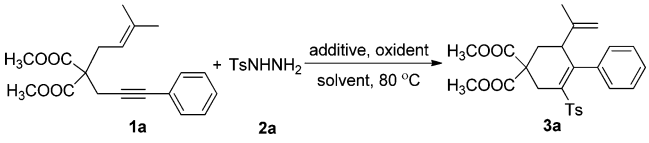
RESULTS AND DISCUSSION

The initial investigation of this iodine-promoted radical cyclization focused on the reaction of 1,6-enyne **1a** with 4-toluenesulfonyl hydrazide **2a** in the presence of TBHP (4.0 equiv, 70 wt % in water) in CH_3CN (1.0 mL) at 80 °C under an argon atmosphere. Gratifyingly, the desired cyclization product **3a** was isolated in 23% yield after 24 h (Table 1, entry 1). With the addition of 20 mol % of KI, the yield of product **3a** increased to 54% (Table 1, entry 2). Subsequent survey on a series of representative solvents revealed that DCE gave the best result, and a comparable result was also obtained in H_2O (Table 1, entries 3−6). Given the continuous demand for green chemistry and the potential value of industrial production, the most low-cost, common and clean resource, water, was finalized as the most suitable solvent for this transformation.

The screening of other iodine-containing reagents showed that iodine performed best and gave the corresponding product **3a** in 76% yield (Table 1, entries 7−10). After subsequent study on various oxidants, TBHP was proved to be the most efficient one for this reaction (Table 1, entries 11−13). By increasing the amount of iodine to 25 mol %, product **3a** was isolated in 85% yield (Table 1, entry 14). An argon atmosphere was essential for high yield (Table 1, entry 15). Finally, the use of **1a** (0.3 mmol), **2a** (0.6 mmol), I_2 (25 mol %) and TBHP (4.0 equiv) in water (1.0 mL) at 80 °C under an argon atmosphere was considered to be the optimized conditions.

With the optimal conditions in hand, the substrate scope of 1,6-enynes was then investigated. As depicted in Table 2, a large variety of sulfonylated products were synthesized through this strategy. The introduction of 4-*tolyl* and 3-*tolyl* groups at alkyne position in 1,6-enynes was found to be suitable for the reaction and gave the corresponding products **3b** and **3c** in good yields, respectively. The 2-*tolyl* substituent was carried out with **2a** slightly decreased the yield of product **3d**, indicating that the reaction was sensitive toward steric hindrance. Electronic effect had a rare influence on the yield of desired products (**3f**−**3k**). Functional groups, such as halogen and cyano group (**3i** and **3l**), could also be compatible in this protocol. Enyne bearing disubstitution (two chloro- group) on the aryl gave the desired product **3q** in 70% yield. The reaction proceeded smoothly for substrates with naphthalenyl and thienyl substituents, affording the products **3r** and **3s** in 52%

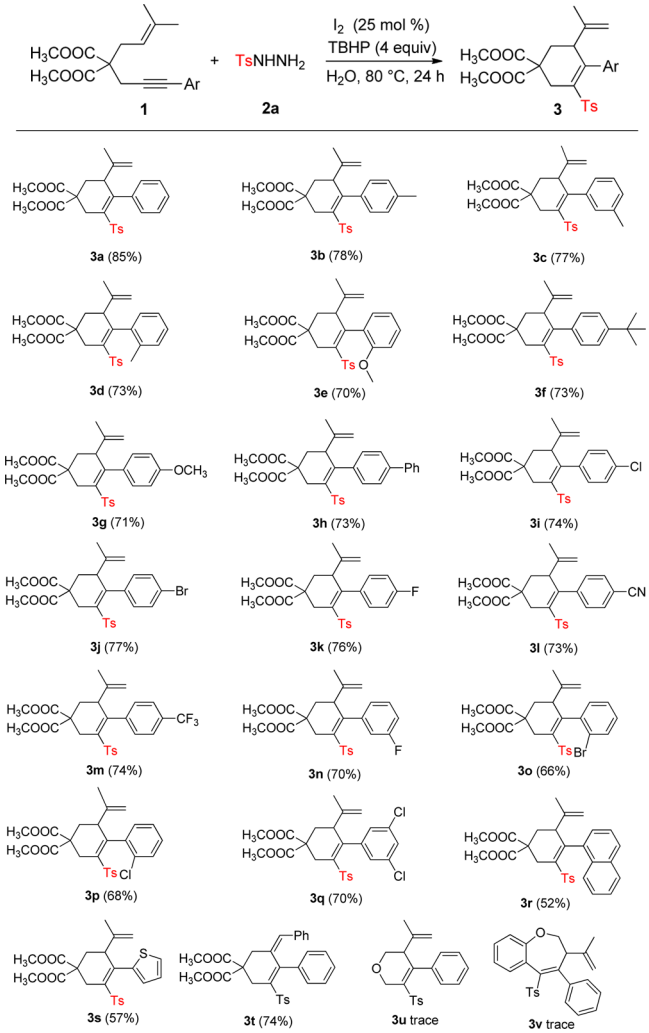
Table 1. Optimization of the Reaction Conditions[a]



entry	solvent	additive	oxidant	yield [%][b]
1	MeCN	–	TBHP	23
2	MeCN	KI	TBHP	54
3	toluene	KI	TBHP	38
4	1,4-dioxane	KI	TBHP	52
5	DCE	KI	TBHP	64
6	H_2O	KI	TBHP	66
7	H_2O	NaI	TBHP	54
8	H_2O	NIS	TBHP	48
9	H_2O	TBAI	TBHP	57
10	H_2O	I_2	TBHP	76
11	H_2O	I_2	DTBP	trace
12	H_2O	I_2	BPO	32
13	H_2O	I_2	$K_2S_2O_8$	51
14[c]	**H_2O**	**I_2**	**TBHP**	**85**
15[d]	H_2O	I_2	TBHP	68
16[e]	H_2O	I_2	TBHP	85

[a]Reaction conditions: **1a** (0.3 mmol), **2a** (0.6 mmol), solvent (1.0 mL), oxidant (1.2 mmol), additive (0.06 mmol) under argon, 24 h, 80 °C. [b]Isolated yields. [c]Additive (0.075 mmol). [d]Under air. [e]Additive (0.12 mmol).

Table 2. Scope of 1,6-Enynes[a]



[a]Reactions were conducted by using **1** (0.3 mmol), **2a** (0.6 mmol), I_2 (25 mmol %), and TBHP (1.2 mmol, 70% in water) in H_2O (1.0 mL) at 80 °C for 24 h under argon.

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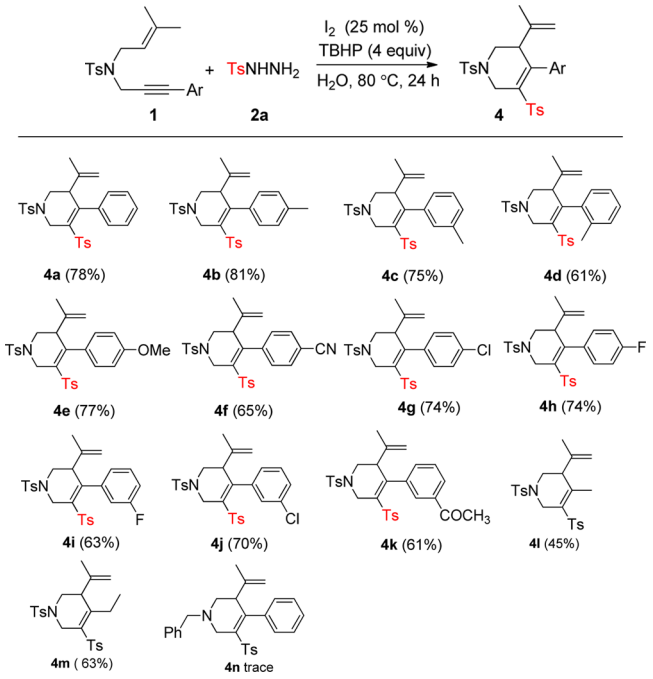
and 57% yield, respectively. Furthermore, the substrate with olefins other than the prenyl type could also be converted into the product **3t** in 74% yield. The *O*-tethered and *phenyl*-tethered substrates failed to provide the desired products. The structure of **3a** was confirmed by X-ray crystal structure analysis (see the Supporting Information).

Encouraged by above results, the reaction of *N*-tethered 1,6-enynes with 4-toluenesulfonyl hydrazide **2a** was also explored under the optimized conditions. As described in Table 3, *N*-

Table 3. Scope of *N*-Tethered 1,6-Enynes[a]

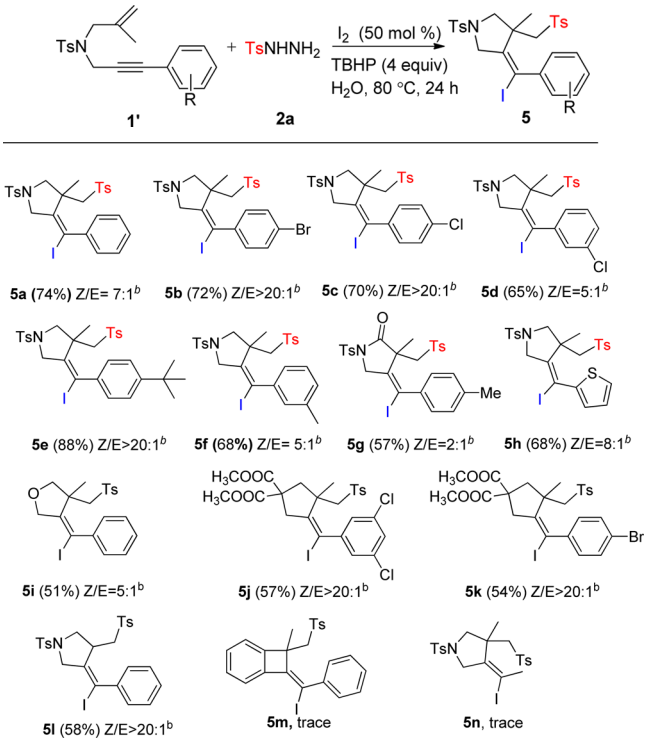


[a]Reactions were conducted by using **1** (0.3 mmol), **2a** (0.6 mmol), I_2 (25 mmol %), and TBHP (1.2 mmol, 70% in water) in H_2O (1.0 mL) at 80 °C for 24 h under argon.

tethered 1,6-enynes with substitution at the *para* (**4b**), *meta* (**4c**) and *ortho* (**4d**) position gave the corresponding products ranging from 61% to 81% yields. Reagents containing an electron-donating (OMe) group (**4e**) or electron-withdrawing groups (**4g**−**4j**) were tolerated. Analogous to Table 3, the steric hindrance influenced the efficiency of this reaction. Acrylonitrile and methyl acrylate delivered the desired products **4f** and **4k** in 65% and 61% yields. *N*-tethered 1,6-enynes with aliphatic acetylenes were also tolerated and gave corresponding products **4l** and **4m** in moderate yield.

On the basis of the above observation about enynes bearing internal alkene, we conceived that the terminal alkene on the substrates could be compatible under the optimal conditions. To our delight, the 5-*exo* cyclization unsubstituted product **5a** was formed in good yield since the terminal C═C bond was the primary reaction site attacked by sulfonyl radical. In this reaction, the sulfonyl and iodine radical were both introduced in enynes. As shown In Table 4, the reaction was matched with a series of substituents of enynes, as the reactions of 4-bromo, 4-chloro, and 3-chloro with **2a** contributed to the corresponding cyclized products (**5b**−**5d**) in moderate yields. Considering that the reaction occurred with high ratios of *Z*/*E* isomer when the *para*-position was substituted, the steric hindrance might be influence on the stereoselectivity. It was noting that the

Table 4. Scope of Terminal Alkene on Enynes[a]



[a]Reactions were conducted by using **1** (0.3 mmol), **2a** (0.6 mmol), I_2 (50 mmol %), and TBHP (1.2 mmol, 70 wt % in water) in H_2O (1.0 mL) at 80 °C for 24 h under argon. [b]The ratios of *Z*/*E* isomers were determined by ^{1}H NMR spectroscopy.

substrate with a methacrylamide group **5g** was tolerated with a low stereoselectivity. The radical cyclization was effective with a 2-*thiophenyl* group **5h** attached to the triple bond with 8.0 *Z*/*E* selectivity. A *O*-tethered enyne **5i** was also a suitable partner to sulfonyl hydrazide. Substrates with geminal substituents **5j** and **5k** proceeded with moderate yield. The product **5l** was successfully obtained with 58% yield. Furthermore, the identity of product **5c** was determined by its X-ray single-crystal structure (see the Supporting Information).

To expand the scope, sulfonyl hydrazide **2** was further examined by treating with 1,6-enynes **1a** in the presence of 40 mol % of I_2. As described in Table 5, electron-withdrawing trifluoromethyl **3ab** and bromo **3ad** groups at the *para*-position of the aryl led to corresponding products in 73% and 79% yields. The electron-donating substitued group **3ae** was tolerated under the conditions. The substrates with naphthalenyl afforded product **3af** in 73% yield. The sulfonyl hydrazide **2aa** furnished the product in slightly lower yield because of instability. Nevertheless, the aliphatic sulfonylhydrazine was not a suitable substrate in this reaction.

In order to reveal the mechanism of this transformation, control experiments were carried out. As shown in Scheme 2, the reaction was significantly inhibited when the reaction was conducted in the presence of 2.0 equiv of 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO). Another radical inhibitor BHT (2,6-di-*tert*-butyl-4-methyl-phenol) was also applied, and the product **3a** was isolated with low yield (47%). This means that a radical pathway might be involved in this transformation. No desired product was observed when 4-toluenesulfonyl chloride **2d** was used instead of hydrazide **2a**.

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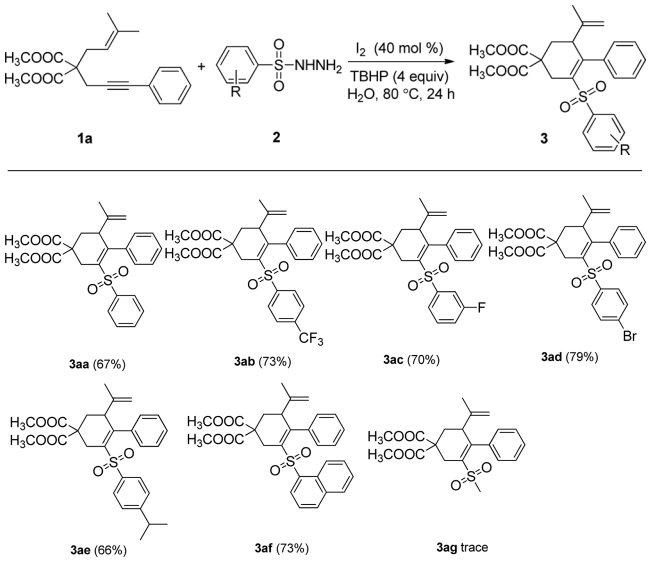
Table 5. Scope of Sulfonyl Hydrazides[a]

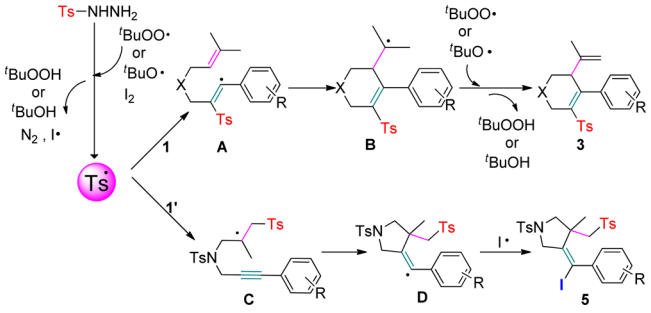


[a]Reactions were conducted by using **1** (0.3 mmol), **2a** (0.6 mmol), I_2 (40 mmol %), and TBHP (1.2 mmol, 70% in water) in H_2O (1.0 mL) at 80 °C for 24 h under argon.

When methyl carbazate **2e** was subject to the cyclization with **1a**, only trace of the product **3z** was observed.

According to above experiments, a mechanism that contained a sulfonyl radical was proposed, as shown in Scheme 3. It was envisioned that, TBHP was decomposed to the *tert*-butoxyl and *tert*-butylperoxy radicals with the initialization of I_2. The reaction of these two radicals and sulfonyl hydrazide gave sulfonyl radical in situ with the releasing of N_2. Subsequently, The addition of the sulfonyl radical and 1,6-enyne **1a** produced intermediate **A**. Intermediate **A** then converted into intermediatd **B** through radical cyclization of a 6-*exo*-trig cyclization process, which generated product **3** after a β-H elimination process. The five-membered product **5** could be obtained through the similar pathway for the construction of C−S and C−I bond in one step.

Scheme 3. Proposed Reaction Mechanism

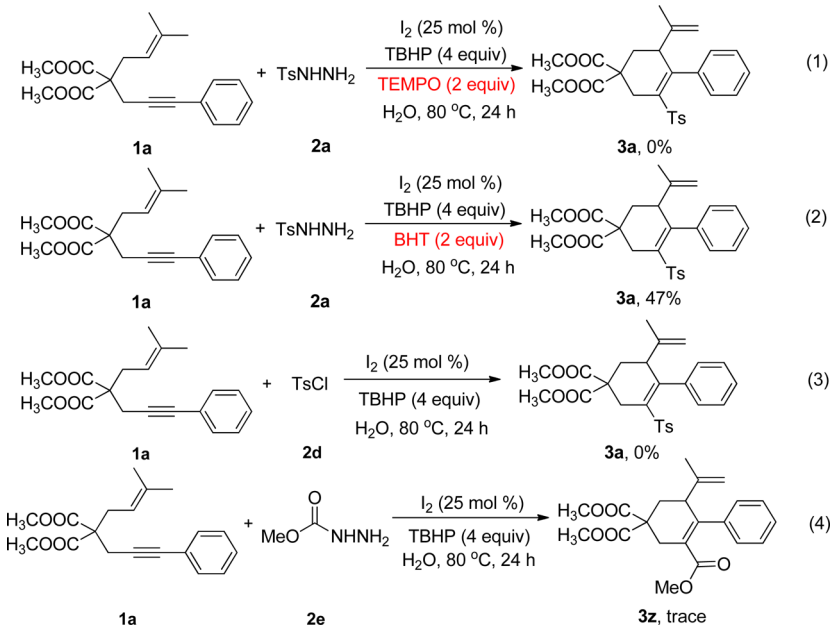


Since the arylsulfonyl radical was an electron-rich radical and the π-bond of alkyne was stronger and less reactive than that of alkene,[17] the addition of radical to C═C bond was considered more preferred under the same steric effects. In turn, the larger sterically hindered group forced the addition to alkyne moiety with low activity. In addition, it is well-known that hexatomic ring was more stability which might be another reason for the formation of product **3**. In conclusion, the selectivity on C═C or C≡C bond of 1,6-enynes attacked by sulfonyl radical was performed in this context.

CONCLUSION

In summary, we have demonstrated a new cyclization contains sulfonylation reaction under convenient conditions of 1,6-enyne for the synthesis of a series of sulfonylated products. This reaction could proceed in water and metal-free conditions in good to excellent yields with C−S and C−I bond formation in one step. Two kinds of cyclization products were obtained due to the control of steric effect. This method allows easy accesses to significant functional sulfones for potential applications in medicinal and organic chemistry.

Scheme 2. Radical Scavenger Experiment



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EXPERIMENTAL SECTION

General Methods. Unless otherwise noted, reactions were carried out under an argon atmosphere. For column chromatography, 200−300 mesh silica gel was employed. Analytical TLC was performed with silica gel GF254 plates. TBHP was used 70 wt % in water. ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) were recorded in $CDCl_3$ using TMS as internal standard. ^{1}H NMR spectra were recorded on 400 MHz in $CDCl_3$ and ^{13}C NMR spectra were recorded on 100 MHz in $CDCl_3$. Chemical shifts (ppm) were recorded with tetramethylsilane (TMS) as the internal reference standard. Multiplicities are given as s (singlet), d (doublet), t (triplet), dd (doublet of doublets), dq (doublet of quartets), q (quartet) or m (multiplet). IR spectra were recorded on a FT-IR spectrometer and only major peaks are reported in cm^{-1}. HR-MS was obtained using a Q-TOF instrument equipped with ESI source. Data collections for crystal structure were performed at room temperature (293 K) using Mo Kα radiation on a Bruker APEXII diffractometer. All compounds were copies of their ^{1}H NMR and ^{13}C NMR spectra are provided in the Supporting Information.

General Procedures for the Synthesis of Substrate 1 and 1′. All of 1,6-enynes was synthesized according to the previous literatures, and the NMR spectroscopy and GC-MS data were in full accordance with the data in the reported literatures.[18]

To a solution of 4-methyl-*N*-(prop-2-ynyl)benzenesulfonamide (1.0 mmol) in CH_2Cl_2(5 mL) was added iPr_2NEt (1.5 mmol) and then cooled to 0 °C in the ice water bath. Methacryloyl chloride (1.2 mmol) was slowly added to the solution at 0 °C and then the mixture was stirred at room temperature for 1 h. The reaction was quenched by water and the aqueous layer was extracted with CH_2Cl_2 (10 mL × 3). The combined organic layers were washed with brine, dried over Na_2SO_4 and concentrated in vacuo. The residue was purified by flash column chromatography to afford product as a white solid.

To a dried Schlenk flask was added $Pd(PPh_3)_2Cl_2$ (0.2 mmol), CuI (0.2 mmol), Iodobenzene (11.0 mmol), C (10.0 mmol) and freshly distilled Et_3N under argon. The resulting mixture was stirred for 16 h at 50 °C. 50 mL of MTBE were added and the mixture filtered. After removal of solvent using rotary evaporator, the residue was purified by flash column chromatography to afford **1′**.

General Procedures for the Synthesis of the Products 3. In an oven-dried tube, **1** (0.3 mmol), sulfonyl hydrazides **2** (0.6 mmol) and I_2 (0.075 mmol) were added and charged with argon more than three times. Pure water (1.0 mL) was added and the TBHP (1.2 mmol) was subsequent injected into the tube. Afterward, the mixture was allowed to stir at 80 °C for 24 h. When the reaction was considered complete, the mixture was extracted with ethyl ether and the combined organic layers were washed with saturated brine, dried over Na_2SO_4. The solvent was removed under vacuo, and the residue was purified with chromatography column (PE−EtOAc, 7:1)on silica gel and recrystallized to afford the product **3** in 85%.

General Procedures for the Synthesis of the Products 5. In an oven-dried tube, **1′** (0.3 mmol), sulfonyl hydrazides **2** (0.6 mmol) and I_2 (0.15 mmol) were added and charged with argon more than three times. Pure water (1.0 mL) was added and the TBHP (1.2 mmol) was subsequent injected into the tube. Afterward, the mixture was allowed to stir at 80 °C for 24 h. When the reaction was considered complete, the mixture was extracted with ethyl ether and the combined organic layers were washed with saturated brine, dried over Na_2SO_4. The solvent was removed under vacuo, and the residue was purified with chromatography column (PE−EtOAc, 6:1) on silica gel and recrystallized to afford the product **5** in 85%.

Dimethyl 6-(prop-1-en-2-yl)-2-tosyl-5,6-dihydro-[1,1′-biphenyl]-4,4(3H)-dicarboxylate ***(3a)***. White solid (119.3 mg, 85% yield); mp 124−126 °C; ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm) 1.56 (s, 3H), 2.04 (dd, J = 10.0 Hz, J = 14.0 Hz, 1H), 2.35 (s, 3H), 2.45−2.51 (m, 1H), 2.97 (dd, J = 3.6 Hz, J = 17.6 Hz, 1H), 3.21−3.26 (m, 1H), 3.54−3.76 (m, 1H), 3.61 (s, 3H), 3.76 (s, 3H), 4.52 (s, 1H), 4.66−4.67 (m, 1H), 7.06−7.12 (m, 3H), 7.19 (t, J = 7.2 Hz, 3H), 7.24 (d, J = 8.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, δ ppm) 171.0, 170.2, 150.7, 143.4, 143.0, 138.0, 136.9, 136.6, 128.9, 127.7, 127.3, 126.9, 116.1, 53.6, 53.0, 52.7, 51.4, 33.2, 31.3, 21.5, 19.4; HRMS (ESI) Calcd for $C_{26}H_{28}O_6S$ [M + Na]$^+$ 491.1499, found 491.1500; IR (cm^{-1}) 2954, 1729, 1598, 1379, 914, 738.

Dimethyl 4′-methyl-6-(prop-1-en-2-yl)-2-tosyl-5,6-dihydro-[1,1′-biphenyl]-4,4(3H)-dicarboxylate ***(3b)***. White solid (112.8 mg, 78% yield); mp 116−118 °C; ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm) 1.56 (s, 3H), 2.03 (dd, J = 10.0 Hz, J = 14.0 Hz, 1H), 2.31 (s, 3H), 2.36 (s, 3H), 2.49 (dd, J = 2.8 Hz, J = 6.8 Hz, 1H), 2.96 (dd, J = 3.6 Hz, J = 17.6 Hz, 1H), 3.21−3.26 (m, 1H), 3.51−3.56 (m, 1H), 3.59 (s, 3H), 3.76 (s, 3H), 4.54 (s, 1H), 4.67 (s, 1H), 6.92 (d, J = 5.6 Hz, 3H), 7.07 (d, J = 8.4 Hz, 3H), 7.26 (d, J = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, δ ppm) 171.0, 170.2, 150.9, 143.3, 143.2, 138.1, 137.0, 136.5, 133.9, 128.8, 127.7, 127.6, 116.0, 53.6, 52.9, 52.6, 51.4, 33.2, 31.2, 21.5, 21.2, 19.4; HRMS (ESI) Calcd for $C_{27}H_{30}O_6S$ [M + Na]$^+$ 505.1655, found 505.1659; IR (cm^{-1}) 2943, 1730, 1378, 900, 811, 676.

Dimethyl 3′-methyl-6-(prop-1-en-2-yl)-2-tosyl-5,6-dihydro-[1,1′-biphenyl]-4,4(3H)-dicarboxylate ***(3c)***. White solid (111.3 mg, 77% yield); mp 125−127 °C; ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm) 1.56 (s, 3H), 2.02−2.08 (m, 1H), 2.15 (s, 3H), 2.36 (s, 3H), 2.45−2.49 (m, 1H), 2.98 (dd, J = 2.8 Hz, J = 17.6 Hz, 1H), 3.20 (s, 1H), 3.59 (s, 1H), 3.65 (s, 3H), 3.77 (s, 3H), 4.52 (s, 1H), 4.67 (s, 1H), 6.03 (s, 1H), 6.97 (d, J = 6.4 Hz, 1H), 7.06 (d, J = 8.0 Hz, 3H), 7.22 (d, J = 7.6 Hz, 2H), 7.27 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, δ ppm) 171.1, 170.3, 150.9, 143.2, 143.0, 138.2, 136.7, 128.8, 128.0, 127.7, 126.9, 116.1, 53.6, 53.0, 52.7, 51.2, 33.1, 31.2, 21.5, 21.3, 19.5; HRMS (ESI) Calcd for $C_{27}H_{30}O_6S$ [M + Na]$^+$ 505.1655, found 505.1664; IR (cm^{-1}) 2953, 1736, 1598, 1378, 791,704.

2′-Methyl-6-(prop-1-en-2-yl)-2-tosyl-5,6-dihydro-[1,1′-biphenyl]-4,4(3H)-dicarboxylate ***(3d)***. White solid (105.5 mg, 73% yield); mp 136−138 °C; ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm) 1.49 (s, 3H), 1.52 (s, 3H), 2,15 (dd, J = 10.8 Hz, J = 13.6 Hz, 1H), 2.37 (s, 3H), 2.47−2.53 (m, 1H), 2.97 (dd, J = 3.6 Hz, J = 17.6 Hz, 1H), 3.14−3.19 (m, 1H), 3.68 (s, 3H), 3.75 (d, J = 9.2 Hz, 1H), 3.78 (s, 3H), 4.50 (s, 1H), 4.62 (s, 1H), 6.82 (d, J = 7.2 Hz, 1H), 6.97−6.98 (m, 1H), 7.03−7.09 (m, 3H), 7.11−7.13 (m, 1H), 7.18 (d, J = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, δ ppm) 171.1, 170.5, 150.3, 143.6, 143.2, 137.6, 137.4, 134.9, 133.8, 131.4, 129.3, 128.8, 127.9, 127.7, 124.2, 115.7, 53.4, 53.1, 52.9, 48.2, 32.6, 31.5, 21.5, 19.9, 18.8; HRMS (ESI) Calcd for $C_{27}H_{30}O_6S$ [M + Na]$^+$ 505.1655, found 505.1660; IR (cm^{-1}) 2956, 1731, 1378, 899, 813, 766, 679.

Dimethyl 2′-methoxy-6-(prop-1-en-2-yl)-2-tosyl-5,6-dihydro-[1,1′-biphenyl]-4,4(3H)-dicarboxylate ***(3e)***. White solid (104.6 mg, 70% yield); mp 138−140 °C; ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm) 1.52 (s, 3H), 2.13 (dd, J = 11.2 Hz, J = 13.2 Hz, 1H), 2.34 (s, 3H), 2.44−2.49 (m, 1H), 2.95 (dd, J = 3.6 Hz, J = 17.6 Hz, 1H), 3.28 (s, 3H), 3.40 (d, J = 3.2 Hz, 1H), 3.69 (s, 3H), 3.73 (d, J = 6.4 Hz, 1H), 3.77 (s, 3H), 4.49 (s, 1H), 4.57 (s, 1H), 6.35 (d, J = 8.4 Hz, 1H), 6.83−6.87 (m, 1H), 7.00 (d, J = 8.0 Hz, 2H), 7.12−7.14 (m, 2H), 7.19 (d, J = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, δ ppm) 171.3, 170.1, 154.4, 149.0, 143.8, 142.7, 137.8, 137.4, 132.7, 129.1, 128.3, 127.5, 124.5, 119.0, 115.2, 109.0, 54.3, 53.6, 53.0, 52.5, 47.3, 32.6, 31.2, 21.4, 19.4; HRMS (ESI) Calcd for $C_{27}H_{30}O_7S$ [M + Na]$^+$ 521.1604, found 521.1608; IR (cm^{-1}) 2956, 1743, 1509, 1378, 1249, 810.

Dimethyl 4′-(tert-butyl)-6-(prop-1-en-2-yl)-2-tosyl-5,6-dihydro-[1,1′-biphenyl]-4,4(3H)-dicarboxylate ***(3f)***. White solid (114.8 mg, 73% yield); mp 126−128 °C; ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm) 1.29 (s, 9H), 1.56 (s, 3H), 2.06 (dd, J = 10.0 Hz, J = 13.6 Hz, 1H), 2.33 (s, 3H), 2.45−2.51 (m, 1H), 2.97 (dd, J = 3.2 Hz, J = 17.6 Hz, 1H), 3.17−3.21 (m, 1H), 3.65 (s, 1H), 3.69 (s, 3H), 3.77 (s, 3H), 3.54 (s, 1H), 3.67 (s, 1H), 6.82−6.99 (m, 3H), 7.06 (s, 2H), 7.14 (d, J = 8.0 Hz, 2H), 7.27 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, δ ppm) 171.1, 170.4, 150.9, 150.2, 143.1, 143.0, 138.3, 137.2, 133.7, 128.7, 127.5, 123.8, 116.0, 53.7, 53.0, 52.7, 51.1, 34.4, 33.3, 31.3, 31.2, 21.5, 19.5; HRMS (ESI) Calcd for $C_{30}H_{36}O_6S$ [M + Na]$^+$ 547.2125, found 547.2128; IR (cm^{-1}) 2960, 1735, 1382, 900, 673.

Dimethyl 4′-methoxy-6-(prop-1-en-2-yl)-2-tosyl-5,6-dihydro-[1,1′-biphenyl]-4,4(3H)-dicarboxylate ***(3g)***. White solid (106 mg, 71% yield); mp 112−116 °C; ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm) 1.56 (s, 3H), 2.00−2.06 (m, 1H), 2.35 (s, 3H), 2.45−2.50 (m, 1H), 2.96 (dd, J = 3.2 Hz, J = 17.6 Hz, 1H), 3.19−3.23 (m, 1H), 3.58 (d, J = 17.6 Hz, 1H), 3.62 (s, 3H), 3.76 (s, 3H), 3.78 (s, 3H), 4.54 (s, 1H),

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4.67 (s, 1H), 6.63−6.72 (m, 3H), 6.85 (d, J = 8.8 Hz, 1H), 7.02−7.09 (m, 2H), 7.25 (d, J = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, δ ppm) 171.0, 170.2, 158.8, 150.6, 143.3, 143.2, 138.2, 136.9, 129.0, 128.8, 127.6, 116.0, 112.4, 55.1, 53.6, 52.9, 52.6, 51.3, 33.2, 31.2, 21.4, 19.4; HRMS (ESI) Calcd for $C_{27}H_{30}O_7S$ [M + Na]$^+$ 521.1604, found 521.1606; IR (cm^{-1}) 2955, 1741, 1378, 899, 678.

Dimethyl 6-(prop-1-en-2-yl)-2-tosyl-5,6-dihydro-[1,1′:4′,1″-terphenyl]-4,4(3H)-dicarboxylate ***(3h)***. White solid (119.1 mg, 73% yield); mp 132−134 °C; ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm) 1.60 (s, 3H), 2.07 (dd, J = 10.0 Hz, J = 13.6 Hz, 1H), 2.35 (s, 3H), 2.48−2.53 (m, 1H), 3.00 (dd, J = 3.2 Hz, J = 17.6 Hz, 1H), 3.27 (s, 1H), 3.61 (s, 1H), 3.66 (s, 3H), 3.78 (s, 3H), 4.57 (s, 1H), 4.69 (s, 1H), 7.04 (d, J = 8.0 Hz, 2H), 7.25−7.27 (m, 3H), 7.34−7.38 (m, 3H), 7.43−7.47 (m, 3H), 7.56 (d, J = 7.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, δ ppm) 171.0, 170.3, 150.4, 143.4, 142.9, 140.6, 140.0, 138.1, 137.2, 135.9, 128.9, 128.8, 127.7, 127.4, 126.9, 125.6, 116.3, 53.6, 53.0, 52.8, 51.2, 33.2, 31.2, 21.5, 19.5; HRMS (ESI) Calcd for $C_{32}H_{32}O_6S$ [M + Na]$^+$ 567.1812, found 567.1817; IR (cm^{-1}) 2959, 1733, 1597, 1380, 898, 673.

Dimethyl 4′-chloro-6-(prop-1-en-2-yl)-2-tosyl-5,6-dihydro-[1,1′-biphenyl]-4,4(3H)-dicarboxylate ***(3i)***. White solid (111.4 mg, 74% yield); mp 126−128 °C; ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm) 1.55 (s, 3H), 1.99−2.05 (m, 1H), 2.38 (s, 3H), 2.45−2.51 (m, 1H), 2.95 (dd, J = 3.6 Hz, J = 17.6 Hz, 1H), 3.17−3.22 (m, 1H), 3.54 (d, J = 17.6 Hz, 1H), 3.61 (s, 3H), 3.76 (s, 3H), 4.53 (s, 1H), 4.69 (s, 1H), 6.89 (d, J = 8.4 Hz, 2H), 7.06−7.13 (m, 3H), 7.17 (dd, J = 2.0 Hz, J = 8.4 Hz, 1H), 7.24−7.29 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, δ ppm) 170.8, 170.1, 149.2, 143.8, 142.6, 137.8, 137.4, 135.3, 133.4, 129.0, 127.6, 127.2, 116.4, 53.5, 53.0, 52.7, 51.2, 33.0, 31.2, 21.5, 19.4; HRMS (ESI) Calcd for $C_{26}H_{27}ClO_6S$ [M + Na]$^+$ 525.1109, found 525.1111; IR (cm^{-1}) 2956, 1730, 1595, 1378, 894, 726, 672.

Dimethyl 4′-bromo-6-(prop-1-en-2-yl)-2-tosyl-5,6-dihydro-[1,1′-biphenyl]-4,4(3H)-dicarboxylate ***(3j)***. White solid (126.1 mg, 77% yield); mp 114−116 °C; ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm) 1.55 (s, 3H), 1.99−2.05 (m, 1H), 2.38 (s, 3H), 2.45−2.50 (m, 1H), 2.95 (dd, J = 3.2 Hz, J = 17.6 Hz, 1H), 3.17−3.21 (m, 1H), 3.54 (d, J = 17.6 Hz, 1H), 3.61 (s, 3H), 3.76 (s, 3H), 4.53 (s, 1H), 4.69 (s, 1H), 6.45−6.84 (m, 1H), 7.13 (dd, J = 8.0 Hz, 2H), 7.23−7.29 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$, δ ppm) 170.9, 170.1, 149.2, 143.8, 142.6, 137.8, 137.4, 135.8, 130.1, 129.7, 129.1, 127.6, 121.6, 116.5, 53.5, 53.0, 52.7, 51.1, 33.0, 31.2, 21.5, 19.4; HRMS (ESI) Calcd for $C_{26}H_{27}BrO_6S$ [M + Na]$^+$ 569.0604, found 569.0610; IR (cm^{-1}) 2957, 1731, 1378, 894, 716, 668.

Dimethyl 4′-fluoro-6-(prop-1-en-2-yl)-2-tosyl-5,6-dihydro-[1,1′-biphenyl]-4,4(3H)-dicarboxylate ***(3k)***. White solid (110.8 mg, 76% yield); mp 130−132 °C; ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm) 1.55 (s, 3H), 2.00−2.06 (m, 1H), 2.37 (s, 3H), 2.45−2.51 (m, 1H), 2.96 (dd, J = 3.2 Hz, J = 17.6 Hz, 1H), 3.17−3.21 (m, 1H), 3.56 (d, J = 17.6 Hz, 1H), 3.62 (s, 3H), 3.78 (s, 3H), 4.53 (s, 1H), 4.68 (s, 1H), 6.82 (s, 3H), 7.11 (d, J = 8.4 Hz, 2H), 7.26 (d, J = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, δ ppm) 170.9, 170.2, 163.2, 160.7, 149.6, 143.7, 142.8, 137.9, 137.4, 132.7, 132.6, 129.0, 127.5, 116.3, 114.1, 113.9. 53.5, 53.0, 52.7, 51.3, 33.0, 31.2, 21.5, 19.4; HRMS (ESI) Calcd for $C_{26}H_{27}FO_6S$ [M + Na]$^+$ 509.1405, found 509.1402; IR (cm^{-1}) 2956, 1729, 1599, 1378, 1144, 896, 677.

Dimethyl 4′-cyano-6-(prop-1-en-2-yl)-2-tosyl-5,6-dihydro-[1,1′-biphenyl]-4,4(3H)-dicarboxylate ***(3l)***. White solid (108 mg, 73% yield); mp 103−105 °C; ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm) 1.55 (s, 3H), 1.99−2.05 (m, 1H), 2.38 (s, 3H), 2.44−2.50 (m, 1H), 2.95 (dd, J = 3.6 Hz, J = 17.6 Hz, 1H), 3.17−3.21 (m, 1H), 3.54 (d, J = 17.6 Hz, 1H), 3.61 (s, 3H), 3.77 (s, 3H), 4.53 (s, 1H), 4.69 (s, 1H), 6.39 (s, 1H), 7.13 (d, J = 8.4 Hz, 3H), 7.28 (d, J = 8.0 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$, δ ppm) 170.6, 170.0, 148.3, 144.2, 142.1, 137.4, 137.3, 129.7, 129.3, 127.7, 126.6, 118.6, 116.8, 111.2, 53.3, 53.1, 52.7, 51.1, 32.8, 31.1, 21.5, 19.4; HRMS (ESI) Calcd for $C_{27}H_{27}NO_6S$ [M + Na]$^+$ 516.1451, found 516.1454; IR (cm^{-1}) 2951, 2228, 1746, 1378, 710.

Dimethyl 6-(prop-1-en-2-yl)-2-tosyl-4′-(trifluoromethyl)-5,6-dihydro-[1,1′-biphenyl]-4,4(3H)-dicarboxylate ***(3m)***. White solid (119 mg, 74% yield); mp 142−144 °C; ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm) 1.56 (s, 3H), 2.05 (dd, J = 10.4 Hz, J = 13.6 Hz, 1H), 2.36 (s, 3H), 2.47−2.52 (m, 1H), 2.96 (dd, J = 3.2 Hz, J = 17.6 Hz, 1H), 3.21 (s, 1H), 3.58 (d, J = 17.6 Hz, 1H), 3.65(s, 3H), 3.78(s, 3H), 4.52 (s, 1H), 4.68 (s, 1H), 6.52(s,1H), 7.08 (d, J = 8.0 Hz, 2H), 7.23−7.26 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$, δ ppm) 170.8, 170.2, 148.8, 143.9, 142.4, 140.7, 137.8, 137.7, 129.6, 129.2, 127.6, 116.7, 53.5, 53.1, 52.8, 51.1, 33.0, 31.1, 21.5, 19.4; HRMS (ESI) Calcd for $C_{27}H_{27}F_3O_6S$ [M + Na]$^+$ 559.1373, found 559.1369; IR (cm^{-1}) 2956, 1740, 1327, 897, 682.

Dimethyl 3′-fluoro-6-(prop-1-en-2-yl)-2-tosyl-5,6-dihydro-[1,1′-biphenyl]-4,4(3H)-dicarboxylate ***(3n)***. White solid (102 mg, 70% yield); mp 148−150 °C ;^{1}H NMR (400 MHz, $CDCl_3$, δ ppm) 1.57 (s, 3H), 2.03 (dd, J = 10.4 Hz, J = 13.6 Hz, 1H), 2.38 (s, 3H), 2.45−2.51 (m, 1H), 2.95 (dd, J = 3.6 Hz, J = 17.6 Hz, 1H), 3.19 (s, 1H), 3.57 (d, J = 17.6 Hz, 1H), 3.63 (s, 3H), 3.77 (s, 3H), 4.54 (s, 1H), 4.69 (s, 1H), 6.87−6.91 (m, 1H), 7.12 (d, J = 8.0 Hz, 3H), 7.27−7.30 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$, δ ppm) 170.9, 170.1, 148.9, 143.8, 142.6, 138.9, 137.7, 137.4, 129.1, 128.6, 128.5, 116.4, 114.4, 114.2, 53.5, 53.1, 52.8, 51.2, 33.0, 31.2, 21.5, 19.4; HRMS (ESI) Calcd for $C_{26}H_{27}FO_6S$ [M + Na]$^+$ 509.1405, found 509.1413; IR (cm^{-1}) 2953, 1730, 1143, 900, 687.

Dimethyl 2′-bromo-6-(prop-1-en-2-yl)-2-tosyl-5,6-dihydro-[1,1′-biphenyl]-4,4(3H)-dicarboxy late ***(3o)***. White solid (108 mg, 66% yield); mp 136−138 °C; ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm) 1.53 (s, 3H), 2.15−2.21 (m, 1H), 2.39 (s, 3H), 2.50−2.56 (m, 1H), 2.98−3.03 (m, 1H), 3.57 (s, 1H), 3.61−3.66 (m, 4H), 3.76 (s, 3H), 4.60 (s, 1H), 4.63 (s, 1H), 7.07−7.12 (m, 1H), 7.14 (d, J = 8.0 Hz, 2H), 7.22 (d, J = 2.4 Hz, 1H), 7.23−7.25 (m, 1H), 7.27 (d, J = 2.4 Hz, 1H), 7.34 (d, J = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, δ ppm) 171.1, 170.0, 148.6, 143.9, 143.0, 137.8, 136.8, 136.4, 133.6, 131.9, 129.2, 129.1, 128.2, 125.7, 120.8, 116.0, 53.1, 53.1, 53.0, 47.0, 32.2, 31.4, 21.6, 19.9; HRMS (ESI) Calcd for $C_{26}H_{27}BrO_6S$ [M + Na]$^+$ 569.0604, found 569.0609; IR (cm^{-1}) 2955, 1734, 1379, 901, 681, 547.

Dimethyl 2′-chloro-6-(prop-1-en-2-yl)-2-tosyl-5,6-dihydro-[1,1′-biphenyl]-4,4(3H)-dicarboxylate ***(3p)***. White solid (102.4 mg, 68% yield); mp 145−147 °C; ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm) 1.54 (s, 3H), 2.17 (dd, J = 2.8 Hz, J = 13.6 Hz, 1H), 2.39 (s, 3H), 2.50−2.55 (m, 1H), 2.98 (dd, J = 3.6 Hz, J = 17.6 Hz, 1H), 3.53 (d, J = 4.8 Hz, 1H), 3.59 (s, 3H), 3.64 (s, 1H), 3.77 (s, 3H), 4.58 (s, 1H), 4.63 (s, 1H), 7.03−7.05 (m, 1H), 7.13 (d, J = 8.0 Hz, 2H), 7.19 (s, 3H), 7.32 (d, J = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, δ ppm) 171.1, 169.9, 147.6, 143.9, 143.0, 138.1, 136.8, 134.5, 133.4, 130.8, 129.1, 129.0, 128.6, 128.0, 125.2, 116.0, 53.3, 53.1, 52.9, 47.3, 32.4, 31.4, 21.6, 19.8; HRMS (ESI) Calcd for $C_{26}H_{27}ClO_6S$ [M + Na]$^+$ 525.1109, found 525.1115; IR (cm^{-1}) 2957, 1733, 1379, 900, 766, 676.

Dimethyl 3′,5′-dichloro-6-(prop-1-en-2-yl)-2-tosyl-5,6-dihydro-[1,1′-biphenyl]-4,4(3H)-dicarboxylate ***(3q)***. White solid (112.6 mg, 70% yield); mp 142−144 °C; ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm) 1.57 (s, 3H), 2.01−2.07 (m, 1H), 2.40 (s, 3H), 2.45−2.51 (m, 1H), 2.92−2.97 (m, 1H), 3.10−3.14 (m, 1H), 3.58−3.63(m, 1H), 3.68 (s, 3H), 3.78 (s, 3H), 4.55 (s, 1H), 4.74 (s, 1H), 6.21 (s, 1H), 6.96 (s, 1H), 7.15 (s, 1H), 7.17−7.18 (m, 2H), 7.30 (d, J = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, δ ppm) 170.8, 170.1, 147.1, 144.3, 142.2, 139.7, 138.8, 137.6, 133.8, 129.3, 127.6, 127.5, 116.9, 53.4, 53.1, 52.9, 50.8, 32.8, 31.0, 21.6, 19.5; HRMS (ESI) Calcd for $C_{26}H_{26}Cl_2O_6S$ [M + Na]$^+$ 559.0719, found 559.0728; IR (cm^{-1}) 2958, 1735, 1380, 808, 589, 549.

Dimethyl 4-(naphthalen-1-yl)-5-(prop-1-en-2-yl)-3-tosylcyclohex-3-ene-1,1-dicarboxylate ***(3r)***. White solid (80.8 mg, 52% yield); mp 152−154 °C; ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm) 1.51 (s, 3H), 2.04 (s, 3H), 2.23−2.29 (m, 1H), 2.54 (dd, J = 4.8 Hz, J = 13.6 Hz, 1H), 3.08 (dd, J = 3.2 Hz, J = 17.6 Hz, 1H), 3.40 (s, 1H), 3.82 (s, 3H), 3.85 (s, 3H), 3.90 (s, 1H), 4.21 (s, 1H), 4.46 (s, 1H), 6.57 (d, J = 7.6 Hz, 2H), 6.83 (d, J = 8.4 Hz, 1H), 6.91 (d, J = 8.0 Hz, 2H), 7.02−7.05 (m, 1H), 7.30 (d, J = 6.8 Hz, 2H), 7.37−7.41 (m, 1H), 7.63 (d, J = 8.0 Hz, 1H), 7.69 (d, J = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, δ ppm) 171.1, 171.0, 149.1, 143.1, 142.9, 139.7, 136.7, 132.8, 132.6, 129.6, 129.4, 128.3, 128.2, 128.1, 127.5, 125.3, 124.8, 124.4, 124.2, 115.8, 53.4, 53.1, 53.0, 49.0, 32.7, 31.4, 21.1, 19.4; HRMS (ESI) Calcd for

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$C_{30}H_{30}O_6S$ [M + Na]$^+$ 541.1655, found 541.1661; IR (cm^{-1}) 2953, 1731, 1378, 803, 704, 671.

Dimethyl 5-(prop-1-en-2-yl)-4-(thiophen-2-yl)-3-tosylcyclohex-3-ene-1,1-dicarboxylate ***(3s)***. White solid (81.0 mg, 57% yield); mp 102−104 °C; ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm)1.61 (s, 3H), 2.06 (dd, J = 9.6 Hz, J = 14.0 Hz, 1H), 2.35 (s, 3H), 2.47−2.52 (m, 1H), 2.99−3.04 (m, 1H), 3.17 (t, J = 6.8 Hz, 1H), 3.63 (d, J = 18.0 Hz, 1H), 3.70 (s, 3H), 3.76 (s, 3H), 4.60 (s, 1H), 4.74 (s, 1H), 6.85−6.87 (m, 1H), 6.94 (d, J = 3.2 Hz, 1H), 7.09 (d, J = 8.0 Hz, 2H), 7.16 (d, J = 4.8 Hz, 1H), 7.32 (d, J = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, δ ppm) 170.9, 170.2, 143.5, 143.4, 143.3, 140.3, 137.6, 136.7, 130.6, 128.9, 127.6, 126.8, 125.8, 116.0, 53.3, 53.0, 52.8, 51.3, 33.1, 31.7, 21.5, 19.4; HRMS (ESI) Calcd for $C_{24}H_{26}O_6S_2$ [M + Na]$^+$ 497.1063, found 497.1070; IR (cm^{-1}) 2956, 1734, 970, 917, 812, 736.

(Z)-Dimethyl-benzylidene-2-tosyl-5,6-dihydro-[1,1′-biphenyl]-4,4(3H)-dicarboxylate ***(3t)***. White solid (115 mg, 74% yield); mp 132−134 °C; ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm) 2.23 (d, J = 8.4 Hz, 2H), 2.37 (s, 3H), 2.66 (t, J = 8.0 Hz, 1H), 2.89−2.94 (m, 1H), 3.50 (s, 3H), 3.77 (s, 3H), 4.94 (d, J = 1.6 Hz, 1H), 6.54 (d, J = 6.0 Hz, 1H), 7.11 (d, J = 7.6 Hz, 4H), 7.17 (s, 3H), 7.26−7.30 (m, 3H), 7.35−7.38 (m, 2H), 7.76 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, δ ppm)170.9, 170.1, 149.8, 143.7, 139.6, 137.8, 137.7, 135.7, 131.0, 129.1, 129.0, 128.4, 128.3, 128.0, 127.8, 127.6, 126.3, 53.6, 53.2, 52.7, 51.3, 41.9, 32.8, 30.7, 21.5; HRMS (ESI) Calcd for $C_{30}H_{28}O_6S$ [M + H]$^+$ 517.1679, found 517.1683; IR (cm^{-1}) 2954, 2923, 1735, 1597, 1262, 1148, 702.

Dimethyl 2-(phenylsulfonyl)-6-(prop-1-en-2-yl)-5,6-dihydro-[1,1′-biphenyl]-4,4(3H)-dicarboxy-late ***(3aa)***. White solid (91.3 mg, 67% yield); mp 125−127 °C; ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm) 1.56 (s, 3H), 2.06 (dd, J = 10.4 Hz, J = 13.6 Hz, 1H), 2.46−2.51 (m, 1H), 2.99 (dd, J = 3.2 Hz, J = 17.6 Hz, 1H), 3.23 (t, J = 6.8 Hz, 1H), 3.58 (s, 1H), 3.62 (s, 3H), 3.77 (s, 3H), 4.52 (s, 1H), 4.67 (s, 1H), 6.87−6.93 (m, 1H), 7.07−7.14 (m, 1H), 7.17 (d, J = 6.8 Hz, 2H), 7.25−7.29 (m, 3H), 7.36 (d, J = 8.0 Hz, 2H), 7.44 (t, J = 7.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, δ ppm) 171.0, 170.2, 151.2, 142.9, 141.0, 136.7, 136.6, 132.6, 128.3, 127.6, 127.3, 116.2, 53.6, 53.1, 52.8, 51.4, 33.1, 31.2, 19.4; HRMS (ESI) Calcd for $C_{25}H_{26}O_6S$ [M + Na]$^+$ 477.1342, found 477.1350; IR (cm^{-1}) 2954, 2850, 1735, 1737, 755, 700, 685.

Dimethyl 6-(prop-1-en-2-yl)-2-((4-(trifluoromethyl)phenyl)-sulfonyl)-5,6-dihydro-[1,1′-bipheny l]-4,4(3H)-dicarboxylate ***(3ab)***. White solid (114.3 mg, 73% yield); mp 132−134 °C; ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm)1.55 (s, 3H), 2.13 (dd, J = 10.4 Hz, J = 14.0 Hz, 1H), 2.46−2.52 (m, 1H), 2.95 (dd, J = 3.6 Hz, J = 17.6 Hz, 1H), 3.13−3.18 (m, 1H), 3.68−3.73 (m, 1H), 3.73 (s, 3H), 3.80 (s, 3H), 4.51 (s, 1H), 4.66 (s, 1H), 6.22 (s, 1H), 6.95−7.03 (m, 1H), 7.14−7.18 (m, 3H), 7.47 (dd, J = 8.8 Hz, J = 13.6 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$, δ ppm)170.8, 170.2, 152.0, 144.6, 142.7, 136.8, 136.3, 134.1, 133.8, 127.9, 127.6, 127.1, 125.3, 125.2, 116.4, 53.5, 53.1, 52.9, 51.1, 32.9, 31.1, 19.4; HRMS (ESI) Calcd for $C_{26}H_{25}F_3O_6S$ [M + Na]$^+$ 545.1216, found 545.1222; IR (cm^{-1}) 2959, 2850, 1744, 1729, 1454, 1380, 1324, 902, 716, 696.

Dimethyl 2-((3-fluorophenyl)sulfonyl)-6-(prop-1-en-2-yl)-5,6-dihydro-[1,1′-biphenyl]-4,4(3H)-dicarboxylate ***(3ac)***. White solid (99.1 mg, 70% yield); mp 138−140 °C; ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm) 1.56 (s, 3H), 2.08 (dd, J = 10.4 Hz, J = 14.0 Hz, 1H), 2.47−2.53 (m, 1H), 2.97 (dd, J = 3.6 Hz, J = 17.6 Hz, 1H), 3.19−3.24 (m, 1H), 3.65 (dd, J = 0.8 Hz, J = 17.6 Hz, 1H), 3.70 (s, 3H), 3.78 (s, 3H), 4.53 (s, 1H), 4.67 (s, 1H), 6.35 (s, 1H), 6.96−6.99 (m, 1H), 7.09−7.12 (m, 3H), 7.14−7.21 (m, 2H), 7.23 (dd, J = 5.2 Hz, J = 8.0 Hz, 1H), 7.27 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, δ ppm) 170.8, 170.2, 163.0, 160.5, 151.9, 142.8, 136.7, 136.4, 130.0, 129.9, 127.5, 123.3, 119.8, 119.6, 116.3, 114.9, 114.7, 53.6, 53.0, 52.8, 51.3, 33.0, 31.1, 19.4; HRMS (ESI) Calcd for $C_{25}H_{25}FO_6S$ [M+NH$_4$]$^+$ 490.1694, found 490.1692; IR (cm^{-1}) 2955, 2851, 1736, 1594, 1436, 1378, 1143, 887, 700, 679.

Dimethyl 2-((4-bromophenyl)sulfonyl)-6-(prop-1-en-2-yl)-5,6-dihydro-[1,1′-biphenyl]-4,4(3H)-dicarboxylate ***(3ad)***. White solid (126.1 mg, 79% yield); mp 143−145 °C; ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm) 1.55 (s, 3H), 2.09 (dd, J = 10.4 Hz, 1H), 2.12−2.51 (m, 1H), 2.94 (dd, J = 3.2 Hz, 1H), 3.17 (s, 1H), 3.62 (d, J = 17.6 Hz, 1H), 3.69 (s, 3H), 3.78 (s, 3H), 4.52 (s, 1H), 4.67 (s, 1H), 6.35 (s, 1H), 7.12 (s, 2H), 7.18 (d, J = 8.4 Hz, 4H), 7.38 (d, J = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, δ ppm) 170.9, 170.2, 151.5, 142.8, 140.1, 136.8, 136.5, 131.5, 129.1, 127.7, 127.5, 127.1, 116.3, 53.5, 53.1, 52.8, 51.3, 33.0, 31.2, 19.4; HRMS (ESI) Calcd for $C_{25}H_{25}BrO_6S$ [M +NH$_4$]$^+$ 550.0893, found 550.0891; IR (cm^{-1}) 2953, 2849, 1753, 1734, 1470, 1378, 1140, 1064, 900, 821, 703, 634.

Dimethyl 2-((4-isopropylphenyl)sulfonyl)-6-(prop-1-en-2-yl)-5,6-dihydro-[1,1′-biphenyl]-4,4 (3H)-dicarboxylate ***(3ae)***. White solid (98.2 mg, 66% yield); mp 145−147 °C; ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm) 1.21 (s, 3H), 1.22 (s, 3H), 1.56 (s, 3H), 2.01−2.07 (m, 1H), 2.46−2.52 (m, 1H), 2.86−2.93 (m, 1H), 2.98 (dd, J = 3.6 Hz, 1H), 3.22−3.27 (m, 1H), 3.61 (s, 3H), 3.61 (dd, J = 1.6 Hz, J = 16.0 Hz, 1H), 3.77 (s, 3H), 4.52 (s, 1H), 4.66 (t, J = 1.2 Hz, 1H), 7.10 (d, J = 8.4 Hz, 4H), 7.16 (t, J = 7.2 Hz, 1H), 7.26 (s, 2H), 7.28 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, δ ppm) 171.1, 170.3, 154.1, 150.6, 143.1, 138.4, 136.9, 136.8, 127.8, 127.2, 127.0, 126.4, 116.1, 53.7, 53.0, 52.7, 51.4, 34.1, 33.2, 31.1, 23.7, 23.6, 19.4; HRMS (ESI) Calcd for $C_{28}H_{32}O_6S$ [M+NH$_4$]$^+$ 514.2258, found 514.2262; IR (cm^{-1}) 2961, 1736, 1600, 1436, 1377, 1153, 902, 700.

Dimethyl 2-(naphthalen-1-ylsulfonyl)-6-(prop-1-en-2-yl)-5,6-dihydro-[1,1′-biphenyl]-4,4(3H)-dicarboxylate ***(3af)***. White solid (110.4 mg, 73% yield); mp 135−137 °C; ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm) 1.56 (s, 3H), 2.03−2.09 (m, 1H), 2.48−2.51 (m, 1H), 3.05 (d, J = 17.6 Hz, 1H), 3.23 (s, 1H), 3.51 (s, 3H), 3.69 (d, J = 17.6 Hz, 1H), 3.77 (s, 3H), 4.51 (s, 1H), 4.65 (s, 1H), 6.35 (s, 1H), 7.09 (s, 3H), 7.47−7.54 (m, 2H), 7.58 (d, J = 7.6 Hz, 1H), 7.69−7.73 (m, 2H), 7.76−7.83 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, δ ppm) 171.0, 170.1, 151.4, 142.9, 137.6, 136.5, 134.7, 131.7, 129.6, 129.3, 128.8, 128.5, 127.6, 127.5, 127.1, 126.8, 122.5, 116.1, 53.6, 53.0, 52.6, 51.4, 33.1, 31.3, 19.4; HRMS (ESI) Calcd for $C_{29}H_{28}O_6S$ [M + H]$^+$ 505.1685, found 505.1689; IR (cm^{-1}) 2950, 2846, 1737, 1622, 1377, 1305, 1262, 1147, 904, 702.

4-Phenyl-3-(prop-1-en-2-yl)-1,5-ditosyl-1,2,3,6-tetrahydropyridine ***(4a)***. White solid (118.6 mg, 78% yield); mp 121−123 °C; ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm) 1.63 (s, 3H), 2.36 (s, 3H), 2.47 (s, 3H), 2.99 (d, J = 12.0 Hz, 1H), 3.05 (s, 1H), 3.53 (d, J = 10.0 Hz, 1H), 3.87 (d, J = 16.8 Hz, 1H), 4.43 (d, J = 16.8 Hz, 1H), 4.59 (s, 1H), 4.80 (s, 1H), 6.76 (s, 2H), 7.06 (d, J = 8.0 Hz, 2H), 7.10−7.14 (m, 2H), 7.19 (d, J = 7.6 Hz, 3H), 7.37 (d, J = 7.6 Hz, 2H), 7.72 (d, J = 7.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, δ ppm) 149.3, 144.1, 144.0, 141.7, 137.7, 136.4, 135.7, 132.9, 129.9, 129.2, 127.8, 127.7, 127.5, 127.3, 116.4, 51.2, 46.8, 45.0, 21.6, 21.5, 21.5; HRMS (ESI) Calcd for $C_{28}H_{29}NO_4S_2$ [M + Na]$^+$ 530.1430, found 530.1438; IR (cm^{-1}) 2918, 2847, 1595, 1444, 1343, 1319, 1168, 892, 700, 670.

3-(Prop-1-en-2-yl)-4-(p-tolyl)-1,5-ditosyl-1,2,3,6-tetrahydropyridine ***(4b)***. White solid (126.6 mg, 81% yield); mp 117−119 °C; ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm)1.63 (s, 3H), 2.31 (s, 3H), 2.37 (s, 3H), 2.47 (s, 3H), 2.94−2.98 (m, 1H), 3.04 (s, 1H), 3.51−3.54 (m, 1H), 3.85 (d, J = 16.8 Hz, 1H), 4.41 (d, J = 17.2 Hz, 1H), 4.59 (s, 1H), 4.80 (s, 1H), 6.66 (d, J = 6.4 Hz, 2H), 6.93 (d, J = 7.6 Hz, 2H), 7.07 (d, J = 8.0 Hz, 2H), 7.21 (d, J = 8.0 Hz, 2H), 7.36 (d, J = 8.0 Hz, 2H), 7.71 (d, J = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, δ ppm)149.5, 144.1, 143.9, 141.9, 137.8, 137.7, 135.5, 133.6, 132.9, 129.9, 129.1, 128.0, 127.7, 127.5, 116.4, 51.2, 46.8, 45.0, 21.6, 21.5, 21.2; HRMS (ESI) Calcd for $C_{29}H_{31}NO_4S_2$ [M + Na]$^+$ 544.1587, found 544.1592; IR (cm^{-1}) 2920, 1596, 1455, 1377, 1356, 1322, 1166, 895, 812, 748.

3-(Prop-1-en-2-yl)-4-(m-tolyl)-1,5-ditosyl-1,2,3,6-tetrahydropyridine ***(4c)***. White solid (117.2 mg, 75% yield); mp 128−130 °C; ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm)1.63 (s, 3H), 2.15 (s, 3H), 2.36 (s, 3H), 2.47 (s, 3H), 2.94−2.98 (m, 1H), 3.03 (s, 1H), 3.55 (dd, J = 3.2 Hz, J = 11.6 Hz, 1H), 3.88 (d, J = 17.2 Hz, 1H), 4.45 (d, J = 17.2 Hz, 1H), 4.59 (s, 1H), 4.81 (s, 1H), 6.37 (s, 1H), 6.65 (s, 1H), 6.99−7.02 (m, 2H), 7.05 (d, J = 7.6 Hz, 2H), 7.17 (d, J = 8.0 Hz, 2H), 7.37 (d, J = 8.0 Hz, 2H), 7.72 (d, J = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, δ ppm)149.5, 144.1, 143.8, 141.8, 137.9, 136.8, 136.3, 135.7, 132.9, 129.9, 129.0, 128.5, 127.7, 127.5, 127.2, 116.4, 51.1, 46.8, 45.0, 21.6, 21.5, 21.4, 21.2; HRMS (ESI) Calcd for $C_{29}H_{31}NO_4S_2$ [M + Na]$^+$ 544.1587, found 544.1594; IR (cm^{-1}) 2923, 2858, 1597, 1459, 1354, 1299, 1167, 1088, 900, 703.

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3-(Prop-1-en-2-yl)-4-(o-tolyl)-1,5-ditosyl-1,2,3,6-tetrahydropyridine ***(4d)***. White solid (95.3 mg, 61% yield); mp 132−134 °C; ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm) 1.63 (s, 3H), 1.74 (s, 3H), 2.38 (s, 3H), 2.47 (s, 3H), 2.86−2.90 (m, 1H), 2.95 (s, 1H), 3.62 (dd, J = 3.2 Hz, J = 11.6 Hz, 1H), 3.86−3.90 (m, 1H), 4.47 (d, J = 17.2 Hz, 1H), 4.59 (s, 1H), 4.84 (s. 1H), 6.69 (d, J = 7.6 Hz, 1H), 6.94−7.00 (m, 2H), 7.09−7.14 (m, 3H), 7.20 (d, J = 8.4 Hz, 2H), 7.38 (d, J = 8.0 Hz, 2H), 7.74 (d, J = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, δ ppm) 149.3, 144.3, 144.1, 141.6, 137.5, 135.6, 135.4, 134.5, 133.0, 130.0, 129.8, 129.6, 129.3, 128.1, 127.8, 124.5, 116.4, 49.5, 46.4, 44.9, 22.1, 21.6, 21.5, 19.3; HRMS (ESI) Calcd for $C_{29}H_{31}NO_4S_2$ $[M + H]^+$ 522.1767, found 522.1772; IR (cm^{-1}) 2920, 2845, 1596, 1455, 1345, 1319, 1168, 1088, 770.

4-(4-Methoxyphenyl)-3-(prop-1-en-2-yl)-1,5-ditosyl-1,2,3,6-tetrahydropyridine ***(4e)***. White solid (124 mg, 77% yield); mp 117−119 °C; ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm) 1.63 (s, 3H), 2.36 (s, 3H), 2.46 (s, 3H), 2.96 (dd, J = 4.8 Hz, J = 12.0 Hz, 1H), 3.03 (s, 1H), 3.51−3.55 (m, 1H), 3.78 (s, 3H), 3.85 (dd, J = 2.0 Hz, J = 16.8 Hz, 1H), 4.47 (d, J = 16.8 Hz, 1H), 4.59 (s, 1H), 4.80 (t, J = 1.2 Hz, 1H), 6.64 (d, J = 9.2 Hz, 2H), 6.70 (d, J = 8.4 Hz, 2H), 7.06 (d, J = 8.4 Hz, 2H), 7.19 (d, J = 8.4 Hz, 2H), 7.36 (d, J = 8.4 Hz, 2H), 7.71 (d, J = 9.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, δ ppm) 159.3, 149.3, 144.0, 143.9, 142.0, 137.9, 135.9, 133.0, 130.0, 129.9, 129.8, 129.7, 129.1, 128.6, 127.7, 127.6, 127.4, 126.4, 116.3, 112.7, 55.1, 51.2, 46.9, 45.1, 21.6, 21.5, 21.5; HRMS (ESI) Calcd for $C_{29}H_{31}NO_5S_2$ $[M + H]^+$ 538.1716, found 538.1718; IR (cm^{-1}) 2922, 1590, 1377, 1322, 1166, 895, 812.

4-(3-(Prop-1-en-2-yl)-1,5-ditosyl-1,2,3,6-tetrahydropyridin-4-yl)benzonitrile ***(4f)***. White solid (103.7 mg, 65% yield); mp 102−104 °C; ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm) 1.62 (s, 3H), 2.42 (s, 3H), 2.48 (s, 3H), 3.03−3.06 (m, 2H), 3.49 (dd, J = 5.6 Hz, J = 13.6 Hz, 1H), 3.88 (d, J = 16.8 Hz, 1H), 4.35 (d, J = 17.2 Hz, 1H), 4.56 (s, 1H), 4.84 (s, 1H), 6.94 (s, 2H), 7.18 (d, J = 8.0 Hz, 2H), 7.27 (d, J = 8.4 Hz, 2H), 7.37 (d, J = 8.0 Hz, 2H), 7.46 (d, J = 8.4 Hz, 2H), 7.70 (d, J = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, δ ppm) 147.0, 144.9, 144.3, 141.5, 141.0, 137.2, 136.9, 132.8, 131.1, 130.0, 129.6, 127.7, 127.5, 118.4, 117.1, 111.8, 50.9, 46.6, 44.9, 21.6, 21.5, 21.5; HRMS (ESI) Calcd for $C_{29}H_{28}N_2O_4S_2$ $[M + H]^+$ 533.1563, found 533.1559; IR (cm^{-1}) 2921, 2228, 1597, 1456, 1344, 1317, 1166, 815.

4-(4-Chlorophenyl)-3-(prop-1-en-2-yl)-1,5-ditosyl-1,2,3,6-tetrahydropyridine ***(4g)***. White solid (120.1 mg, 74% yield); mp 152−154 °C; ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm) 1.62 (s, 3H), 2.39 (s, 3H), 2.47 (s, 3H), 2.97−3.01 (m, 2H), 3.51 (dd, J = 5.6 Hz, J = 14.0 Hz, 1H), 3.87 (d, J = 16.8 Hz, 1H), 4.40 (d, J = 17.2 Hz, 1H), 4.58 (s, 1H), 4.82 (s, 1H), 6.71 (d, J = 6.0 Hz, 2H), 7.09−7.13 (m, 4H), 7.23 (d, J = 8.4 Hz, 2H), 7.36 (d, J = 8.0 Hz, 2H), 7.71 (d, J = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, δ ppm) 147.9, 144.4, 144.2, 141.5, 137.5, 136.5, 134.9, 134.0, 132.9, 129.9, 129.3, 127.7, 127.5, 127.4, 116.7, 51.0, 46.7, 44.9, 21.5; HRMS (ESI) Calcd for $C_{28}H_{28}ClNO_4S_2$ $[M + H]^+$ 542.1221, found 542.1224; IR (cm^{-1}) 2918, 1634, 1595, 1488, 1379, 1316, 1166, 1087, 890, 737.

4-(4-Fluorophenyl)-3-(prop-1-en-2-yl)-1,5-ditosyl-1,2,3,6-tetrahydropyridine ***(4h)***. White solid (116.6 mg, 74% yield); mp 145−147 °C; ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm) 1.62 (s, 3H), 2.38 (s, 3H), 2.47(s, 3H), 2.98 (d, J = 4.8 Hz, 1H), 3.01 (s, 1H), 3.48−3.53 (m, 1H), 3.88 (d, J = 16.8 Hz, 1H), 4.41 (d, J = 17.2 Hz, 1H), 4.58 (s, 1H), 4.82 (s, 1H), 6.75 (s, 2H), 6.80−6.84 (m, 2H), 7.11(d, J = 8.0 Hz, 2H), 7.22 (d, J = 8.4 Hz, 2H), 7.37 (d, J = 8.4 Hz, 2H), 7.72 (d, J = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, δ ppm) 163.5, 161.1, 148.3, 144.3, 144.2, 141.6, 137.7, 136.5, 132.8, 132.3, 132.2, 130.0, 129.3, 127.8, 127.4, 116.6, 114.5, 114.3, 51.2, 46.8, 45.1, 21.6, 21.6, 21.5; HRMS (ESI) Calcd for $C_{28}H_{28}FNO_4S_2$ $[M + Na]^+$ 548.1336, found 548.1342; IR (cm^{-1}) 2920, 1633, 1597, 1503, 1342, 1169, 902, 818.

4-(3-Fluorophenyl)-3-(prop-1-en-2-yl)-1,5-ditosyl-1,2,3,6-tetrahydropyridine ***(4i)***. White solid (99.2 mg, 63% yield); mp 150−152 °C; ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm) 1.63 (s, 3H), 2.39 (s, 3H), 2.47 (s, 3H), 2.97−3.01 (m, 2H), 3.50−3.55 (m, 1H), 3.86−3.91 (m, 1H), 4.42 (d, J = 17.2 Hz, 1H), 4.58 (s, 1H), 4.83 (s, 1H), 6.33 (s, 1H), 6.65 (s, 1H), 6.89−6.94 (m, 1H), 7.12 (d, J = 8.0 Hz, 3H), 7.25 (d, J = 8.0 Hz, 2H), 7.37 (d, J = 8.4 Hz, 2H), 7.71 (d, J = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, δ ppm) 147.6, 144.5, 144.2, 141.5, 138.5, 138.4, 137.5, 136.6, 130.0, 129.9, 129.4, 129.0, 128.9, 127.8, 127.5, 116.7, 114.9, 114.7, 51.0, 46.7, 44.9, 21.6, 21.5, 21.5; HRMS (ESI) Calcd for $C_{28}H_{28}FNO_4S_2$ $[M + H]^+$ 526.1517, found 526.1522; IR (cm^{-1}) 2923, 1596, 1341, 1147, 896, 746, 695.

4-(3-Chlorophenyl)-3-(prop-1-en-2-yl)-1,5-ditosyl-1,2,3,6-tetrahydropyridine ***(4j)***. White solid (113.6 mg, 70% yield); mp 176−178 °C; ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm) 1.63 (s, 3H), 2.39 (s, 3H), 2.47 (s, 3H), 2.99 (d, J = 8.0 Hz, 2H), 3.52−3.57 (m, 1H), 3.89 (d, J = 17.2 Hz, 1H), 4.45 (d, J = 17.2 Hz, 1H), 4.58 (s, 1H), 4.83 (s, 1H), 6.43 (s, 1H), 6.82 (s, 1H), 7.10−7.14 (m, 3H), 7.17−7.21 (m, 3H), 7.36 (d, J = 8.0 Hz, 2H), 7.71 (d, J = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, δ ppm) 147.4, 144.5, 144.2, 141.3, 138.1, 137.4, 136.9, 133.3, 133.0, 129.9, 129.4, 128.7, 127.9, 127.7, 127.4, 116.7, 50.9, 46.6, 44.9, 21.6, 21.5; HRMS (ESI) Calcd for $C_{28}H_{28}ClNO_4S_2$ $[M + H]^+$ 542.1221, found 542.1226; IR (cm^{-1}) 2923, 1595, 1352, 1309, 1184, 1167, 893, 796, 739.

1-(3-(3-(Prop-1-en-2-yl)-1,5-ditosyl-1,2,3,6-tetrahydropyridin-4-yl)phenyl)ethanone ***(4k)***. White solid (100.5 mg, 61% yield); mp 140−142 °C; ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm) 1.63 (s, 3H), 2.34 (s, 3H), 2.48 (d, J = 1.6 Hz, 6H), 2.99- 3.05 (m, 2H), 3.56 (d, J = 2.8 Hz, J = 11.6, 1H), 3.88 (dd, J = 2.0 Hz, J = 17.2 Hz, 1H), 4.45 (d, J = 17.2 Hz, 1H), 4.60 (s, 1H), 4.83 (s, 1H), 7.07 (d, J = 8.0 Hz, 2H), 7.18 (d, J = 8.4 Hz, 3H), 7.31 (t, J = 7.6 Hz, 2H), 7.38 (d, J = 8.0 Hz, 2H), 7.72 (d, J = 8.4 Hz, 2H), 7.82 (d, J = 7.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, δ ppm) 197.1, 148.2, 144.4, 144.2, 141.4, 137.6 136.9, 136.8, 136.1, 132.9, 130.0, 129.9, 129.7, 129.4, 127.7, 127.4, 126.6, 126.4, 116.8, 51.0, 46.7, 44.9, 26.4, 21.6, 21.5, 21.4; HRMS (ESI) Calcd for $C_{30}H_{31}NO_5S_2$ $[M+NH_4]^+$ 567.1982, found 567.1995; IR (cm^{-1}) 2925, 1683, 1600, 1377, 1343, 1301, 1148, 1088, 910, 670.

4-Methyl-3-(prop-1-en-2-yl)-1,5-ditosyl-1,2,3,6-tetrahydropyridine ***(4l)***. White oil (60 mg, 45% yield); mp 148−150 °C; ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm) 1.64 (s, 3H), 2.01 (s, 3H), 2.44 (s, 3H), 2.44 (s, 3H), 2.87 (s, 1H), 2.92 (dd, J = 5.2 Hz, J = 12.0 Hz, 1H), 3.25 (dd, J = 4.4 Hz, J = 11.6 Hz, 1H), 3.76 (d, J = 16.4 Hz, 1H), 4.04 (d, J = 16.4 Hz, 1H), 4.62 (s, 1H), 4.92 (s, 1H), 7.34 (t, J = 8.4 Hz, 4H), 7.64 (d, J = 8.0 Hz, 2H), 7.76 (d, J = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, δ ppm) 147.6, 144.6, 144.0, 142.4, 138.0, 132.7, 132.2, 129.9, 129.8, 127.6, 126.9, 116.1, 50.4, 46.4, 45.2, 21.5, 21.5, 20.6, 18.7. HRMS (ESI) Calcd for $C_{23}H_{27}NO_4S_2$ $[M + H]^+$ 446.1454, found 446.1456; IR (cm^{-1}) 2925, 2856, 2257, 1597, 1348, 1164, 910, 815.

4-Ethyl-3-(prop-1-en-2-yl)-1,5-ditosyl-1,2,3,6-tetrahydropyridine ***(4m)***. White solid (81 mg, 63% yield); mp 152−154 °C; ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm) 0.91 (t, J = 7.6 Hz, 3H), 1.67 (s, 3H), 1.85−1.93 (m, 1H), 2.43 (s, 3H), 2.45 (s, 3H), 2.76−2.80 (m, 1H), 3.04 (s, 1H), 3.06−3.15 (m, 1H), 3.42−3.46 (m, 1H), 3.70 (d, J = 16.4 Hz, 1H), 4.07 (d, J = 16.4 Hz, 1H), 4.56 (s, 1H), 4.90 (s, 1H), 7.34 (t, J = 8.4 Hz, 4H), 7.65 (d, J = 8.0 Hz, 2H), 7.77 (d, J = 7.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, δ ppm) 153.1, 144.6, 140.0, 138.4, 132.8, 131.7, 129.9, 129.8, 127.6, 126.9, 115.9, 46.5, 45.2, 24.7, 21.6, 21.5, 21.0, 13.1. HRMS (ESI) Calcd for $C_{24}H_{29}NO_4S_2$ $[M + H]^+$ 460.1611, found 460.1614; IR (cm^{-1}) 2975, 2938, 2257, 1597, 1452, 1348, 1165, 912, 815, 733.

(Z)-4-(Iodo(phenyl)methylene)-3-methyl-1-tosyl-3-(tosylmethyl)-pyrrolidine ***(5a)***. White solid (137.9 mg, 74% yield); Z/E = 7:1; ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm) Z isomer: 1.22 (s, 3H), 2.44 (s, 3H), 2.48 (s, 3H), 2.87 (d, J = 14.4 Hz, 1H), 3.02 (d, J = 14.0 Hz, 1H), 3.42 (d, J = 10.0 Hz, 1H), 3.71 (d, J = 10.0 Hz, 1H), 3.77 (d, J = 10.0 Hz, 1H), 3.96 (d, J = 15.6 Hz, 1H), 7.07−7.11 (m, 2H), 7.28 (d, J = 7.6 Hz, 4H), 7.32−7.38 (m, 1H), 7.40 (d, J = 8.0 Hz, 2H), 7.50 (d, J = 8.4 Hz, 2H), 7.75 (d, J = 8.0 Hz, 2H); ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm) E isomer: 1.26 (s, 3H), 2.45 (s, 3H), 2.46 (s, 3H), 2.87 (d, J = 14.4 Hz, 1H), 3.15 (d, J = 10.0 Hz, 1H), 3.42 (d, J = 10.0 Hz, 1H), 3.71 (d, J = 10.0 Hz, 1H), 3.82 (d, J = 6.4 Hz, 1H), 4.01 (d, J = 10.0 Hz, 1H), 7.07−7.11 (m, 2H), 7.28 (d, J = 7.6 Hz, 4H), 7.32−7.38 (m, 1H), 7.40 (d, J = 8.0 Hz, 2H), 7.61 (d, J = 8.0 Hz, 2H), 7.81 (d, J = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, δ ppm) Z isomer: 148.1, 144.7, 144.1, 142.4, 138.0, 131.7, 130.0, 129.9, 129.8, 128.7, 128.5, 128.1, 127.7, 127.3, 127.0, 94.1, 61.5, 60.6, 60.0, 46.7, 23.9, 21.6, 21.6;

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HRMS (ESI) Calcd for $C_{27}H_{28}INO_4S_2$ $[M + H]^+$ 622.0577, found 622.0583; IR (cm^{-1}) 2923, 1598, 1311, 1228, 1153, 689.

(Z)-4-((4-Bromophenyl)iodomethylene)-3-methyl-1-tosyl-3-(tosylmethyl)pyrrolidine ***(5b)***. White solid (151 mg, 72% yield); *Z*/*E* > 20:1; ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm) Z isomer: 1.19 (s, 3H), 2.46 (s, 3H), 2.48 (s, 3H), 2.84 (d, *J* = 14.0 Hz, 1H), 3.03 (d, *J* = 14.2 Hz, 1H), 3.38 (d, *J* = 10.0 Hz, 1H), 3.78 (m, 2H), 3.93 (d, *J* = 15.2 Hz, 1H), 6.97 (d, *J* = 8.0 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.40 (d, *J* = 8.0 Hz, 4H), 7.52 (d, *J* = 8.4 Hz, 2H), 7.75 (d, *J* = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, δ ppm) Z isomer: 149.1, 144.8, 144.2, 141.3, 138.0, 131.7, 129.9, 129.4, 128.1, 127.3, 122.9, 92.2, 61.6, 60.6, 60.0, 46.8, 23.9, 21.6; HRMS (ESI) Calcd for $C_{27}H_{27}BrINO_4S_2$ $[M + H]^+$ 699.9682, found 699.9677; IR (cm^{-1}) 2924, 2844, 1597, 1483, 1338, 1317, 1160, 1088, 1047, 869, 814, 763, 665.

(Z)-4-((4-Chlorophenyl)iodomethylene)-3-methyl-1-tosyl-3-(tosylmethyl)pyrrolidine ***(5c)***. White solid (137.6 mg, 70% yield); *Z*/*E* > 20:1; ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm) Z isomer: 1.19 (s, 3H), 2.45 (s, 3H), 2.48 (s, 3H), 2.85 (d, *J* = 14.0 Hz, 1H), 3.05 (d, *J* = 14.0 Hz, 1H), 3.37 (d, *J* = 9.6 Hz, 1H), 3.78 (m, 2H), 3.93 (d, *J* = 15.2 Hz, 1H), 7.03 (d, *J* = 8.4 Hz, 2H), 7.25 (d, *J* = 9.2 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 7.40 (d, *J* = 8.0 Hz, 2H), 7.53 (d, *J* = 8.4 Hz, 2H), 7.75 (d, *J* = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, δ ppm) Z isomer: 149.1, 144.9, 144.2, 144.1, 140.8, 138.0, 134.7, 131.8, 129.9, 129.2, 128.8, 128.1, 127.3, 92.3, 61.6, 60.6, 60.0, 46.8, 23.9, 21.6; HRMS (ESI) Calcd for $C_{27}H_{27}ClINO_4S_2$ $[M + H]^+$ 656.0187, found 656.0182; IR (cm^{-1}) 2924, 2855, 1594, 1487, 1348, 1315, 1156, 1089, 817, 758, 665.

(Z)-4-((3-Chlorophenyl)iodomethylene)-3-methyl-1-tosyl-3-(tosylmethyl)pyrrolidine ***(5d)***. White solid (127.7 mg, 65% yield); *Z*/*E* = 5:1; ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm) Z isomer: 1.22 (s, 3H), 2.46 (s, 3H), 2.50 (s, 3H), 2.89 (d, *J* = 14.0 Hz, 1H), 3.07 (d, *J* = 14.0 Hz, 1H), 3.39 (d, *J* = 9.6 Hz, 1H), 3.80−3.85 (m, 2H), 3.96 (d, *J* = 15.6 Hz, 1H), 7.00−7.05 (m, 1H), 7.09−7.11 (m, 1H), 7.26 (d, *J* = 5.2 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.42 (d, *J* = 7.6 Hz, 2H), 7.57 (d, *J* = 8.4 Hz, 2H), 7.78 (d, *J* = 8.0 Hz, 2H); ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm) E isomer: 1.46 (s, 3H), 2.48 (3H), 2.50 (s, 3H), 3.56 (d, J = 14.4 Hz, 1H), 3.63 (d, *J* = 11.2 Hz, 1H), 3.67 (d, *J* = 7.6 Hz, 1H), 4.14 (dd, *J* = 7.2 Hz, *J* = 14.4 Hz, 2H), 4.51 (d, *J* = 10.8 Hz, 1H), 7.00−7.05 (m, 1H), 7.09−7.11 (m, 1H), 7.26 (d, *J* = 5.2 Hz, 2H), 7.42 (d, *J* = 7.6 Hz, 2H), 7.46 (d, *J* = 8.0 Hz, 2H), 7.62 (d, *J* = 8.0 Hz, 2H), 7.79 (d, *J* = 5.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, δ ppm) Z + E isomer: 149.1, 145.4, 144.8, 144.7, 144.7, 144.2, 143.9, 140.9, 138.0, 137.7, 134.4, 134.2, 133.2, 131.7, 131.7, 130.3, 129.9, 129.9, 129.9, 129.8, 128.9, 128.4, 128.1, 127.9, 127.7, 127.5, 127.3, 126.3, 126.0, 125.7, 91.6, 61.5, 60.7, 60.3, 59.9, 59.8, 58.5, 46.8, 46.8, 26.2, 24.0, 21.7, 21.6, 21.6, 21.5; HRMS (ESI) Calcd for $C_{27}H_{27}ClINO_4S_2$ $[M + H]^+$ 656.0187, found 656.0188; IR (cm^{-1}) 2923, 2844, 1597, 1488, 1338, 1317, 1160, 1088, 1048, 765, 750, 675.

(Z)-4-((4-(tert-Butyl)phenyl)iodomethylene)-3-methyl-1-tosyl-3-(tosylmethyl)pyrrolidine ***(5e)***. White solid (178.7 mg, 88% yield); *Z*/*E* > 20:1; ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm) Z isomer: 1.27 (s, 3H), 2.42 (s, 3H), 2.48 (s, 3H), 2.75 (d, *J* = 14.0 Hz, 1H), 2.91 (d, *J* = 14.0 Hz, 1H), 3.59 (s, 2H), 3.69 (d, *J* = 15.2 Hz, 1H), 4.03 (d, *J* = 15.2 Hz, 1H), 7.01 (d, *J* = 7.2 Hz, 2H), 7.25 (d, *J* = 7.6 Hz, 4H), 7.44 (m, 4H), 7.77 (d, *J* = 7.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, δ ppm) Z isomer: 152.0, 148.1, 144.6, 144.0, 139.4, 138.1, 131.8, 129.9, 129.8, 128.1, 127.4, 127.2, 125.3, 94.3, 61.7, 60.5, 60.0, 46.6, 34.7, 31.1, 24.4, 21.6, 21.5; HRMS (ESI) Calcd for $C_{31}H_{36}INO_4S_2$ $[M + H]^+$ 678.1203, found 678.1204; IR (cm^{-1}) 2925, 1597, 1315, 1228, 1147, 900, 689.

(Z)-4-(Iodo(m-tolyl)methylene)-3-methyl-1-tosyl-3-(tosylmethyl)-pyrrolidine ***(5f)***. White solid (129.5 mg, 68% yield); *Z*/*E* = 5:1; ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm) Z isomer: 1.23 (s, 3H), 2.23 (s, 3H), 2.44 (s, 3H), 2.48 (s, 3H), 2.87 (d, *J* = 14.0 Hz, 1H), 2.99 (d, *J* = 14.4 Hz, 1H), 3.45 (d, *J* = 9.6 Hz, 1H), 3.67 (d, *J* = 9.6 Hz, 1H), 3.74 (d, *J* = 15,2 Hz, 1H), 3.97 (d, *J* = 15.2 Hz, 1H), 6.89 (d, *J* = 7.6 Hz, 2H), 7.06 (d, *J* = 7.6 Hz, 1H), 7.17 (t, *J* = 7.6 Hz, 1H), 7.28 (d, *J* = 8.8 Hz, 2H), 7.40 (d, *J* = 8.0 Hz, 2H), 7.50 (d, *J* = 8.0 Hz, 2H), 7.76 (d, *J* = 8.0 Hz, 2H); ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm) E isomer: 1.35 (s, 3H), 2.32 (s, 3H), 2.45 (s, 3H), 2.46 (s, 3H), 2.97 (d, *J* = 14.4 Hz, 1H), 3.14 (d, *J* = 10.0 Hz, 1H), 3.52 (d, *J* = 10.0 Hz, 1H), 3.67 (d, *J* = 9.6 Hz, 1H), 3.86 (d, *J* = 14.4 Hz, 1H), 4.00 (d, *J* = 12.8 Hz, 1H), 6.84 (d, *J* = 11.2 Hz, 2H), 7.06 (d, *J* = 7.6 Hz, 1H), 7.17 (t, *J* = 7.6 Hz, 1H), 7.28 (d, *J* = 8.8 Hz, 2H), 7.35 (d, *J* = 7.6 Hz, 2H), 7.62 (d, *J* = 8.0 Hz, 2H), 7.81 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, δ ppm) Z + E isomer: 147.8, 145.5, 145.2, 144.8, 144.6, 144.5, 144.4, 144.1, 143.8, 143.0, 142.2, 138.5, 138.2, 138.1, 137.9, 131.7, 131.3, 129.9, 129.8, 129.7, 129.5, 128.6, 128.4, 128.2, 128.2, 128.1, 128.0, 127.7, 127.5, 127.2, 124.8, 123.9, 94.2, 90.3, 61.6, 60.5, 60.1, 59.7, 59.6, 59.2, 53.7, 53.0, 46.6, 46.6, 24.2, 24.0, 22.2, 21.6, 21.5, 21.3, 21.2; HRMS (ESI) Calcd for $C_{28}H_{30}INO_4S_2$ $[M + H]^+$ 636.0734, found 636.0732; IR (cm^{-1}) 2923, 1597, 1453, 1380, 1348, 1317, 1161, 1089, 1045, 815, 744, 665.

(Z)-4-(Iodo(p-tolyl)methylene)-3-methyl-1-tosyl-3-(tosylmethyl)-pyrrolidin-2-one ***(5g)***. White solid (111 mg, 57% yield); *Z*/*E* = 2:1; ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm) Z isomer: 1.10 (s, 3H), 2.33 (s, 3H), 2.40 (s, 3H), 2.42 (s, 3H), 3.07 (d, *J* = 14.4 Hz, 1H), 3.24 (d, *J* = 14.4 Hz, 1H), 4.62 (dd, *J* = 14.4 Hz, *J* = 35.2 Hz, 2H), 7.05−7.15 (m, 2H), 7.22 (s, 3H), 7.27−7.28 (m, 2H), 7.33−7.42 (m, 3H), 8.07 (d, *J* = 8.4 Hz, 2H); ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm) E isomer: 1.61 (s, 3H), 2.37 (s, 3H), 2.41(s, 3H), 2.43 (s, 3H), 3.41 (d, *J* = 14.0 Hz, 1H), 4.46 (d, *J* = 14.0 Hz, 1H), 4.36 (dd, *J* = 14.4 Hz, *J* = 24.8 Hz, 2H), 7.05−7.15 (m, 2H), 7.20 (s, 3H), 7.28−7.30 (m, 2H), 7.33−7.42 (m, 3H), 7.97 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, δ ppm) Z + E isomer: 174.9, 174.7, 145.3, 145.2, 144.7, 144.7, 143.2, 141.8, 138.9, 138.3, 138.1, 138.0, 137.6, 136.1, 134.1, 133.9, 129.7, 129.7, 129.6, 129.3, 129.2, 129.2, 129.1, 129.0, 128.2, 127.5, 127.4, 127.3, 125.5, 123.9, 98.9, 94.1, 63.1, 59.7, 58.7, 51.5, 50.1, 49.9, 25.6, 22.4, 21.8, 21.7, 21.6, 21.6, 21.4, 21.4; HRMS (ESI) Calcd for $C_{28}H_{28}INO_5S_2$ $[M + H]^+$ 650.0526, found 650.0532; IR (cm^{-1}) 2920, 1735, 1560, 1378, 1348, 1319, 1045, 815, 665.

(Z)-4-(Iodo(thiophen-2-yl)methylene)-3-methyl-1-tosyl-3-(tosylmethyl)pyrrolidine ***(5h)***. White solid (127.9 mg, 68% yield); *Z*/*E* = 8:1; ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm) Z isomer: 1.34 (s, 3H), 2.45 (s, 3H), 2.48 (s, 3H), 3.12 (dd, *J* = 14.4 Hz, *J* = 22.8 Hz, 2H), 3.40 (d, *J* = 10.0 Hz, 1H), 3,72−3.78 (m, 2H), 3.92 (d, *J* = 15.2 Hz, 1H), 6.89−6.92 (m, 2H), 7.30−7.33 (m, 3H), 7.39 (d, *J* = 8.0 Hz, 2H), 7.60 (d, *J* = 8.4 Hz, 2H), 7.74 (d, *J* = 8.4 Hz, 2H); ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm) E isomer: 1.68 (s, 3H), 2.43 (s, 3H), 2.46 (s, 3H), 3.12 (dd, *J* = 14.4 Hz, *J* = 22.8 Hz, 2H), 3.61 (d, *J* = 14.4 Hz, 1H), 3,72−3.78 (m, 2H), 3.86 (d, *J* = 14.4 Hz, 1H), 6.94−6.98 (m, 2H), 7.30−7.33 (m, 3H), 7.39 (d, *J* = 8.0 Hz, 2H), 7.66 (d, *J* = 8.4 Hz, 2H), 7.79 (d, *J* = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, δ ppm) Z isomer: 152.6, 144.8, 144.2, 143.7, 138.1, 131.7, 129.9, 129.9, 128.1, 127.8, 127.5, 127.1, 126.9, 84.3, 61.0, 60.9, 60.0, 47.1, 23.5, 21.6; HRMS (ESI) Calcd for $C_{25}H_{26}INO_4S_3$ $[M + H]^+$ 628.0141, found 628.0147; IR (cm^{-1}) 2923, 1597, 1450, 1347, 1314, 1159, 1088, 1045, 814, 757.

(Z)-4-(Iodo(phenyl)methylene)-3-methyl-3-(tosylmethyl)-tetrahydrofuran ***(5i)***. White oil (71.7 mg, 51% yield); *Z*/*E* = 5:1; ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm) 1.21 (s, 3H), 1.26 (s, 3H), 2.43 (s, 3H), 2.47 (s, 3H), 2.93 (d, *J* = 14.0 Hz, 1H), 3.08 (d, *J* = 14.0 Hz, 1H), 3.57 (d, *J* = 14.4 Hz, 1H), 3.82 (d, *J* = 9.2 Hz, 1H), 3.99 (d, *J* = 9.2 Hz, 1H), 4.16 (d, *J* = 1.6 Hz, 2H), 4.34−4.37 (m, 2H), 4,43 (d, *J* = 14.4 Hz, 1H), 4.59 (d, *J* = 9.2 Hz, 1H), 7.14 (d, *J* = 7.2 Hz, 2H), 7.18 (d, *J* = 7.2 Hz, 2H), 7.27 (d, *J* = 7.2 Hz, 2H), 7.38 (d, *J* = 8.0 Hz, 2H), 7.29−7.32 (m, 3H), 7.29−7.32 (m, 3H), 7.55 (d, *J* = 8.0 Hz, 2H), 7.88 (d, *J* = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, δ ppm) 151.6, 144.6, 142.3, 138.2, 129.8, 128.6, 128.5, 128.0, 127.3, 90.1, 80.3, 79.6, 61.4, 22.9, 21.6; HRMS (ESI) Calcd for $C_{20}H_{21}IO_3S$ $[M + H]^+$ 469.0329, found 469.0334; IR (cm^{-1}) 2928, 2854, 1560, 1316, 1147, 1086, 946, 738.

(E)-Dimethyl 4-((3,5-dichlorophenyl)iodomethylene)-3-methyl-3-(tosylmethyl)cyclopentane-1,1-dicarboxylate ***(5j)***. Yellow solid (111 mg, 57% yield); *Z*/*E* > 20:1; ^{1}H N MR (400 MHz, $CDCl_3$, δ ppm) 1.14 (s, 3H), 2.44 (s, 3H), 2.77 (d, *J* = 14.4 Hz, 1H), 2.92 (d, *J* = 14.0 Hz, 1H), 3.07 (d, *J* = 14.0 Hz, 1H), 3.26−3.38 (m, 2H), 3.42 (d, *J* = 14.4 Hz, 1H), 3.80 (s, 3H), 3.81 (s, 3H), 7.04 (d, *J* = 1.6 Hz, 2H), 7.22−7.23 (m, 1H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.60 (d, *J* = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, δ ppm) 172.1, 171.9, 154.2, 146.1, 144.9, 138.7, 135.0, 130.2, 128.6, 127.5, 90.3, 64.1, 56.9, 53.6, 53.4,

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50.6, 47.6, 46.7, 27.7, 21.9; HRMS (ESI) Calcd for $C_{25}H_{26}Cl_2IO_6S$ $[M + H]^+$ 650.9866, Found 650.9869; IR (cm^{-1}) 2954, 2927, 2257, 1735, 1559, 1149, 910, 734.

*(E)-Dimethyl 4-((4-bromophenyl)iodomethylene)-3-methyl-3-(tosylmethyl)cyclopentane-1,1-dicarboxylate (**5k**).* White solid (107 mg, 54% yield); Z/E > 20:1; ^1H NMR (400 MHz, $CDCl_3$, δ ppm) 1.13 (s, 3H), 2.45 (s, 3H), 2.80−2.86 (m, 2H), 3.02 (d, J = 14.4 Hz, 1H), 3.21−3.30 (m, 2H), 3.37 (d, J = 14.4 Hz, 1H), 3.80 (s, 3H), 3.81 (s, 3H), 7.01 (d, J = 8.0 Hz, 2H), 7.31 (d, J = 8.0 Hz, 2H), 7.38 (d, J = 8.0 Hz, 2H), 7.51 (d, J = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, δ ppm) 172.0, 171.7, 153.1, 144.5, 142.3, 138.4, 131.5, 129.8, 127.2, 122.3, 92.7, 63.9, 56.7, 53.3, 53.1, 50.1, 47.5, 46.3, 27.1, 21.6; HRMS (ESI) Calcd for $C_{25}H_{26}BrIO_6S$ $[M + H]^+$ 660.9751, found 660.9756; IR (cm^{-1}) 2953, 2929, 2850, 1734, 1265, 1150, 1086, 816, 713.

*(Z)-3-(Iodo(phenyl)methylene)-1-tosyl-4-(tosylmethyl)pyrrolidine (**5l**).* White solid (105 mg, 58% yield); Z/E > 20:1; ^1H NMR (400 MHz, $CDCl_3$, δ ppm) 2.44 (s, 3H), 2.47 (s, 3H), 2.64 (d, J = 14.0 Hz, 1H), 2.87−2.95 (m, 1H), 3.14 (s, 1H), 3.43−3.47 (m, 1H), 3.73 (d, J = 15.6 Hz, 1H), 3.88 (dd, J = 2.4 Hz, J = 10.8 Hz, 1H), 3.98 (d, J = 15.6 Hz, 1H), 6.96 (d, J = 7.2 Hz, 2H), 7.16 (t, J = 7.2 Hz, 2H), 7.21 (d, J = 7.6 Hz, 3H), 7.33 (d, J = 8.0 Hz, 2H), 7.39 (d, J = 8.0 Hz, 2H), 7.77 (d, J = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, δ ppm) 144.7, 144.2, 144.1, 141.3, 135.3, 132.0, 129.9, 129.9, 128.8, 128.5, 128.0, 127.6, 127.3, 93.7, 59.1, 56.2, 53.5, 36.9, 21.6, 21.5. HRMS (ESI) Calcd for $C_{26}H_{26}INO_4S_2$ $[M + H]^+$ 608.0421, found 608.0427; IR (cm^{-1}) 2922, 2859, 1735, 1596, 1166, 815.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.5b02161.

X-ray structures. (CIF)
X-ray structures. (CIF)
Copies of ^1H NMR, ^{13}C NMR spectra. (PDF)

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Notes

The authors declare no competing financial interest.

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